

INSTITUT FÜR KERNCHEMIE
UNIVERSITÄT MAINZ

**JAHRESBERICHT
2008**



Juli 2009

Kernchemie im Internet

Das Institut für Kernchemie der Universität Mainz ist mit einer Homepage im World Wide Web vertreten. Unter der Adresse

<http://www.kernchemie.uni-mainz.de>

finden Sie aktuelle Informationen zum Institut, seinen Mitarbeitern, den Lehrveranstaltungen und den Forschungsaktivitäten.

Die in diesem Bericht vorgelegten Ergebnisse stammen zum Teil aus noch nicht abgeschlossenen Arbeiten und sind daher als vorläufige Mitteilung zu bewerten.



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Herausgeber: Frank Rösch
Mainz, im Juli 2009

Vorwort

Der Jahresbericht 2008 gibt einen Überblick über die vielfältigen wissenschaftlichen Aktivitäten des Instituts für Kernchemie und listet die Ergebnisse in Form von Publikationen, Konferenzbeiträgen, Dissertationen, Diplom- und Staatsexamensarbeiten auf. Zusätzlich beschreibt die Beiträge der Hochschullehrer und wissenschaftlichen Mitarbeiter des Instituts in der Lehre und Weiterbildung sowie zu verschiedenen Strahlenschutzkursen. Schließlich wird der Status der technischen Einrichtungen des Instituts dargelegt. Der wissenschaftliche Bericht gliedert sich in die Forschungsschwerpunkte:

- Kern- und Radiochemie im Sinne grundlegender Fragestellungen,
- Radiopharmazeutische Chemie und Anwendung radiochemischer Methoden mit lebenswissenschaftlicher Zielsetzung,
- Hochempfindliche und selektive Analytik für physikalische, umweltrelevante, technische und biologische Probleme.

Das Jahr 2008 markiert grundsätzliche Umstrukturierungsprozesse innerhalb der Universität wie auch innerhalb des Instituts für Kernchemie. In die neuen Schwerpunktbildungen der Universität ist das Institut für Kernchemie mit mehreren Arbeitsgruppen involviert - in das Forschungszentrum „Elementarkräfte und mathematische Grundlagen“ (J.V. Kratz, W. Nörtershäuser) und in den Forschungsschwerpunkt „SOPTRANS“ (F. Rösch).

Parallel zu den wissenschaftlichen Forschungen erlebt das Institut eine seit seiner Gründung nie dagewesene Metamorphose. Das Institut wird im Zeitraum 2008/2009 drei Juniorprofessuren besetzen. Herr Plonka-Spehr trat im April 2008 seine von der Carl-Zeiss-Stiftung vergebene Juniorprofessur an. Seine Forschungen betreffen die am TRIGA-Reaktor Mainz erzeugten ultrakalten Neutronen.

Der im Jahr 2006 begonnene Bau eines neuen Institutsflügels als Ersatz für die Räume im M-Haupt wurde 2008 erfolgreich abgeschlossen. Am 27.10.2008 fand die offizielle Einweihung statt. Mitarbeitern und Studenten stehen nun hochmoderne und den aktuellen Vorschriften des Arbeits- und Strahlenschutzes entsprechende Forschungslabore und Praktikumsplätze zur Verfügung.

Aus der Radiopharmazeutischen Chemie kommen zwei hochpotente Neurotransmitteranaloge, mit denen auch eine Namensgebung initiiert wird: [^{18}F]MH.MZ und [^{18}F]PR07.MZ zur hochselektiven Visualisierung der serotonergen bzw. dopaminergen Signaltransduktion offenbaren ihre Mainzer Abstammung als Extension „MZ“. Der Helmholtz-Nachwuchsgruppe von W. Nörtershäuser ist es erstmals gelungen, den Kernladungsradius des Ein-Neutronen Halokerns Beryllium-11 zu messen. Dazu wurde die kollineare Laserspektroskopie, deren Leistungsfähigkeit vor fast 30 Jahren am TRIGA-Reaktor Mainz demonstriert wurde, mit einem Frequenzkamm kombiniert.

Vom 15.-18.04.2008 hat das Institut die 40. Jahrestagung des Fachverbandes für Strahlenschutz ausgerichtet. Die etwa 100 Teilnehmer diskutierten die Themen „Ausbildung, Weiterbildung und Lehre im Strahlenschutz“.

Am 17. Dezember 2008 beging das Institut ein sehr prominent besuchtes Festsymposium anlässlich des 70. Jahrestages der Entdeckung der Kernspaltung. Auf diesem Symposium wurde Herrn Dr. Norbert Trautmann die „Honorarprofessur“ der Johannes Gutenberg-Universität verliehen.

Die wissenschaftlichen Arbeiten im Institut wurden wiederum vielfältig finanziell gefördert - vor allem vom Land Rheinland-Pfalz über die Johannes Gutenberg-Universität, vom Bundesministerium für Bildung und Forschung, vom Bundesministerium für Wirtschaft und Technologie, von der Deutschen Forschungsgemeinschaft, vom Deutschen Akademischen Austauschdienst, von der Gesellschaft für Schwerionenforschung in Darmstadt und durch die Helmholtz-Gemeinschaft. Förderungen durch die Europäische Gemeinschaft (FP 6) erfolgten im Rahmen der Vorhaben EMIL und ACTINET. Den Fördernden sei herzlich gedankt.

Mainz, den 3. Juli 2009



Prof. Dr. Frank Rösch

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Im Jahr 2008 wurde eine Broschüre erstellt, die in komprimierter Form Informationen zu den Forschungen am Institut und am TRIGA-Reaktor Mainz darlegt. Diese liegt dem gedruckten Bericht bei und ist auch unter (<http://www.kernchemie.uni-mainz.de>) abrufbar.

Erweiterungsbau Kernchemie, Sommer 2008



Zusammenfassung

- A. Kernchemie**
- B. Radiopharmazeutische Chemie / Kernchemie in den Lebenswissenschaften**
- C. Radiochemische Analytik für umweltrelevante und technische Probleme**
- D. Technische Einrichtungen**
- E. Veröffentlichungen, Vorträge, Lehrveranstaltungen**

Summary

- A. Nuclear and Radiochemistry**
- B. Radiopharmaceutical Chemistry / Nuclear Chemistry for Life Sciences**
- C. Radiochemical Analytics for Environment and Technology**
- D. Technical Facilities**
- E. Publications, Conference Contributions, Teaching Activities**

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Wissenschaftliche Mitarbeiter

Amayri	S.	Herrmann	G.	Nörtershäuser	W.
Beyerlein	F.	<i>(emeritiert)</i>		Piel	M.
Buda	R. A.	Jahn	M.	Plonka-Spehr	Ch.
Cerchietti	L.	Keller	H.	Reich	T.
Denschlag	J.O.	Kiselev	O.	Rösch	F.
<i>(pensioniert)</i>		Kratz	J. V.	Trautmann	N.
Eberhardt	K.	Kratz	K.-L.	Wiehl	N.
Geppert	Chr.	<i>(pensioniert)</i>		Wu	T.
Hampel	G.	Neugart	R.		

Diplomanden, Doktoranden und Staatsexamenskandidaten

Andjelkovic	Z.	Klimach	T.	Scheid	N.
Betzel	T.	Krämer	J.	Schieferstein	H.
Biegi	C.	Kraft	A.	Schönberger.	M.
Burchhardt	C.	Kramer	V.	Schütz	Ch.
Capito	T.	Krieger	A.	Smorra	Ch.
Cazan	R.M.	Lang	T.	Stöbener	N.
Dierking	S.	Lauer	T.	Streicher	B.
Eppard	E.	Loktionova	N.	Tiedemann	D.
Even	J.	Meister	M.	Vicente Vilas	V.
Fellner	M.	Moderegger	D.	Vogtländer	L.
Fröhlich	D.	Nothhelfer	M.	Wunderlich	T.
Gromm	E.	Ölcer	A.	Zakova	M.
Hampel	J.	Radchenko	V.	Zenner	J.
Herth	M.	Reich	Ta.	Zimny	M.
Heß	T.	Reichert	P.	Zoller	F.
Hild	D.	Riß	P.		
		Rossi	D.		

Angestellte

Breuel	J.	Keim	H. J.	Onasch	I.
Drebert	J.	Keller	O.	Peil	A.
Gerhardt	T.	Kling	H. O.	Praast	B.
Handwerker	C.	Krille	U.	Sach-Muth	P.
Heiser	A.	Lehr	G.	Schmidt	A.
Höhnemann	S.	Liebe	D.	Schmidt	H.-M.
Hubrath	J.	Mendel	M.	Thörle-Pospiech	P.
Janzen	V.	Müller	J.	Widera	R.
Jera	R.	Nähler	A.	Zauner	S.

Gäste 2008

Afaj, A.	Ministry of Science and Technology, Baghdad, Irak
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Altarev, I.	TU München
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Stöppler, R.	TU München
Thews, O.	Institut für Physiologie und Pathophysiologie, Mainz
Urban, M.	Physik Department, TU München
Weidenauer, P.	Areva NP, Erlangen
Yoon, Da In	DAAD-IASTE-Programm
Zimontkowski, B.	Nuklearmedizinische Praxis zum Frankfurter Tor, Berlin

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- A20 Prototyping of DSSD detectors for the EXL/R³B collaboration
B. Streicher, P. Egelhof, V. Eremin, J.V. Kratz, X.C.Le, M. Mutterer, N. Pietralla, M.von Schmid, and the EXL and R³B collaborations
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- B. Radiopharmazeutische Chemie / Kernchemie in den Lebenswissenschaften
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Förderungen der im Jahresbericht enthaltenen Arbeiten erfolgten durch folgende Institutionen:

Land Rheinland-Pfalz:

Kompetenzzentrum „Neuro-PET“ des Landes Rheinland-Pfalz

Stiftung Rheinland-Pfalz für Innovation „Ankopplung einer Laserspektroskopie- und Massenspektrometrieapparatur für kurzlebige Radionuklide an dem Mainzer TRIGA-Reaktor“

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Johannes Gutenberg-Universität Mainz:

Forschungsfonds der Johannes Gutenberg-Universität Mainz

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Bundesministerium für Bildung und Forschung (BMBF) im Rahmen des Vorhabens „Schwerste Elemente: Chemische Mikrotrennapparaturen und TASCA“

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Deutsche Forschungsgemeinschaft im Rahmen des Vorhabens „Synthese von hochaffinen ¹⁸F-markierten Liganden zur Untersuchung von NMDA-Rezeptoren mittels Positronen-Emissions-Tomographie (PET)

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Deutsche Forschungsgemeinschaft im Rahmen des Vorhabens „Determination of the isotopic composition of trace amounts of actinides in environmental micro-particles by Resonance Ionisation Mass Spectrometry (RIMS) of Sputtered Neutrals (SN)“

Deutsche Forschungsgemeinschaft im Rahmen des Vorhabens „Determination of ^{236}U in Environmental Samples by High Resolution Resonance Ionization Mass Spectrometry“

Deutscher Akademischer Austauschdienst (DAAD):

DAAD im Rahmen des Internationalen Studentenaustausch-Programms zwischen der „Johannes Gutenberg-Universität Mainz und der State University of New York at Stony Brooks/dem Brookhaven National Laboratory“

GSI Helmholtzzentrum für Schwerionenforschung GmbH:

GSI Helmholtzzentrum für Schwerionenforschung im Rahmen der Zusammenarbeitsvereinbarungen zwischen Wissenschaftlern von Hochschulen und der GSI

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Europäische Gemeinschaft:

Europäische Gemeinschaft im Rahmen des Vorhabens „European Molecular Imaging Laboratories“

Europäische Gemeinschaft im Rahmen des Network of Excellence „ACTINET“

Boehringer-Ingelheim-Stiftung:

Boehringer-Ingelheim-Stiftung für das Projekt „Borbestimmung in Gewebeprobe im Rahmen der Entwicklung eines Behandlungsprotokolls für die Bor-Neutronen-Einfangtherapie an einer autotransplantierten Leber“

A.

Kernchemie

Nuclear- and Radiochemistry

First production of spin polarized neutrons at the UCN source at channel C of the reactor TRIGA Mainz

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Introduction: Ultra cold neutrons (UCN) with velocities < 7 m/s are a unique tool to address many questions of modern particle physics like e.g. the matter- antimatter asymmetry in our Universe or the understanding of the primordial baryogenesis directly after the Big Bang. Experiments with UCN, in this frame work, search for a non-zero electric dipole moment of the neutron or the precise determination of the neutron lifetime.

Our group in Mainz participates in such experiments, where the polarization of UCN and the analyzing of the spin orientation after certain storage time play an essential role. A brief summary of our work with polarized UCN is presented here:

Experiment at the new UCN source in Mainz: For the first time polarized ultra cold neutrons were produced. For that purpose a magnetized iron foil was placed in the UCN beam. This foil consists of a 500 nm Fe layer on 25 μm Al. The effective Fermi potential of the magnetic saturated iron depends on the orientation of the neutron spin relative to this magnetisation, thus working as a spin filter. UCN with velocities less than 4 m/s are being reflected. Between 4 m/s and 8 m/s, only UCN with an anti-parallel alignment of spin and magnetic field are transmitted. Neutrons with velocities greater than 8 m/s are transmitted regardless of their spin orientation. The detection of the spin orientation is achieved in the same way.

An essential tool for the work with polarized neutrons is a spin-flipper. The working principle of a broadband adiabatic spin-flipper can be found e.g. in [1]. It consists of a magnetic gradient field perpendicular to the direction of flight and an induced radiofrequency parallel to the direction of flight.

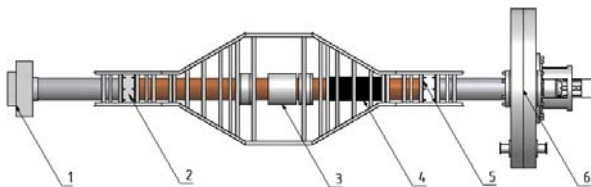


Figure 1. Setup for a polarization measurement.

(1) UCN detector, (2) analyzer foil, (3) grounded Al shielding to prevent RF in the second gradient, (4) RF coil, (5) polarizing foil, (6) Chopper. UCN come from the right side.

The polarization and the spin-flipp probability are velocity dependent. Therefore a chopper divides the continuous UCN beam into bunches and simultaneously starts a trigger signal on each bunch. The velocity is derived by measuring the UCN time of flight together with the length of the flight path.

Figure 1 shows a schematic draft of the experiment, as it was performed in January 2008 at the TRIGA Mainz.

Results: As shown in fig. 2, the measured polarisation depends on the velocity. It is zero for velocities greater than 8 m/s and comes close to 1 (i.e. 100%) for UCN slower than 6.8 m/s.

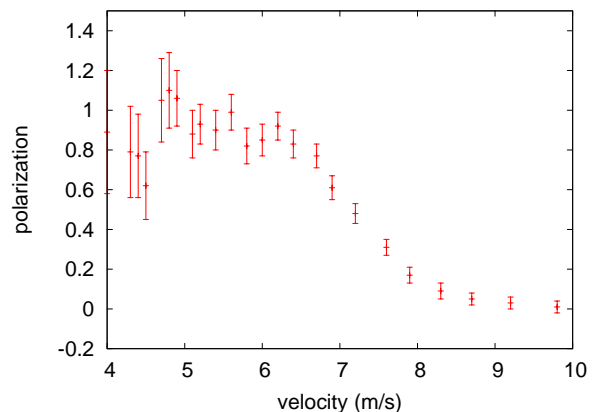


Figure 2. Measured polarization. For velocities less than 6.8 m/s the efficiency of the setup is close to 100 %.

The efficiency of the whole setup is given by the product of the efficiencies of the single components: Polarizer, spin-flipper and analyzer. Since the average value for UCN between 4.9 m/s and 6.9 m/s is $95 (\pm 3) \%$, one can assume that the efficiency of the single components (i.e. the polarization) is even higher.

References

- [1] Grigoriev S.V., et. al. Peculiarities of the construction and application of a broadband adiabatic spin-flipper of cold neutrons. Nuclear Instruments and Methods in Physics Research, 1997; 451-456

Aufbau eines Experiments zur Messung einer möglichen elektrischen Ladung des freien Neutrons.

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Wir bauen zur Zeit ein Experiment auf zur Bestimmung einer möglichen elektrischen Ladung des Neutrons. Eine nicht verschwindende Ladung des Neutrons ist konsistent mit der Erhaltung der elektrischen Ladung, der Baryonen- und der Leptonenzahl [1]. Sie würde implizieren, dass die Erhaltung der Baryonenzahl und die Erhaltung der elektrischen Ladung keine unabhängigen Symmetrien sind. In der ersten Phase wurde mit einer Testapparatur ein „proof-of-principle“ erreicht. Der Aufbau ist in Abb. 1 dargestellt.



Abbildung 1. Erste Ausbauphase des Ladungsexperiments, angelehnt an [2]

Das Prinzip der Messung ist der Aufbau einer „Kamera“ für ultrakalte Neutronen (UCN) mit einer Geschwindigkeit < 7 m/s.

Die gesamte Apparatur befindet sich in einer Vakuumkammer (1). Über einen Neutronenleiter (2) gelangen ultrakalte Neutronen in die Apparatur. Der UCN-Strahl durchquert das Eingangsgitter (3) und wird dort fragmentiert. Der Strahl durchläuft den Weg zwischen zwei UCN-Leitern von einer Länge von 50 cm (4a und 4b), wird zwischen oberer und unterer Platte reflektiert und gelangt schließlich zu einem Spiegel (6). Dieser Spiegel ist senkrecht aus der Bildebene hinaus gekrümmt und hat einen Krümmungsradius von 50 cm. Von diesem Spiegel werden die UCN wieder zurückreflektiert und gelangen zu einem Ausgangsgitter (7) mit einer identischen Gitterkonstante wie der des Eingangsgitters. Hinter diesem Ausgangsgitter befindet sich ein Detektor zum Nachweis der Neutronen. Ausgangsgitter und Detektor sind mit Hilfe eines Servomotors (8) senkrecht aus der Bildebene hinaus verschiebbar.

Entweder das UCN passiert einen Spalt des Eingangsgitters, um dann hinter dem Spalt des Ausgangsgitters zur Zählrate beizutragen, oder es trifft auf einen Steg des Ausgangsgitters und wird absorbiert.

In verschiedenen Versuchen wurde die Abhängigkeit der Zählrate von der Verschiebung des Ausgangsgitters gemessen.

Es ergibt sich in Abhängigkeit von der Verschiebung des Ausgangsgitters (grating13) eine Modulation der Zählrate (Abb. 2).

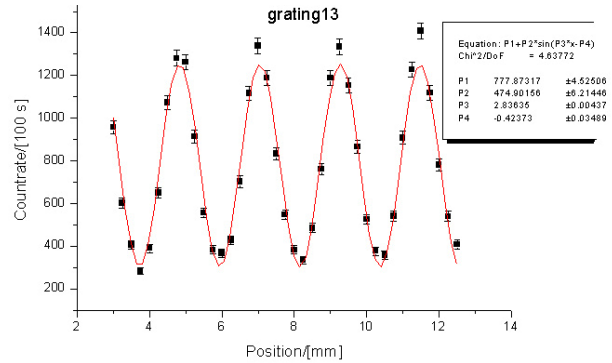


Abbildung 2. Abhängigkeit der Zählrate von der Verschiebung des Ausgangsgitters.

Ziel des Experimentes soll es sein, zwischen zwei Titanelektroden (5), die sich senkrecht zur Flugrichtung der UCN befinden, eine Hochspannung von etwa 100kV anzulegen. Sollte das Neutron eine Ladung haben, würde sich bei Anlegen eines elektrischen Feldes eine Ablenkung der Neutronen und damit eine Veränderung des Ausgangssignals nachweisen lassen.

In die zu bestimmende Größe geht die genaue Flugzeit der Neutronen zwischen den beiden Gittern ein. Dazu wurde Anfang 2009 ein Choppersystem entwickelt, das in die Vakuumkammer eingebaut wird und mit dem die genaue Flugzeit der Neutronen vom Eingangsgitter bis zum Detektor bestimmt werden kann.

Dieses Choppersystem wird in einer zweiten Ausbauphase im März 2009 getestet. Während dieser Zeit sollen auch verschiedene Einflüsse auf die Zählrate durch eine Verkippung der optischen Komponenten des Systems untersucht werden.

Wir erwarten eine Verbesserung der Sensitivität auf die elektrische Ladung des Neutrons um eine Größenordnung auf $10^{-22} q_e$.

References

- [1] G.Feinberg and M.Goldhaber, Proc. Nat. Acad. Sci. USA 45 (1959) 1301
- [2] Yu.V.Borisov et al., Zh. Tekh. Fiz. 58 (1988) 951-958

Messung der effektiven Lebensdauer und der Verluste von Ultrakalten Neutronen (UCN) in einer Speicherkammer aus Sitall-Glaskeramik

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Einleitung: Nach einem Theorem von Sakharov [1] könnte ein von Null abweichender und über die Vorhersagen des Standardmodells der Elementarteilchenphysik hinausgehender Wert für das elektrische Dipolmoment d_n des Neutrons einen Erklärungsansatz für die beobachtete Materie-Antimaterie-Asymmetrie in unserem Universum liefern. Die präziseste Grenze für diesen Wert ($d_n < 3 \cdot 10^{-26} e \cdot \text{cm}$) liefert zurzeit das Experiment [2]. Dieses wird von einer europäischen Kollaboration unter Mainzer Beteiligung am Paul-Scherrer Institut (Villigen/Schweiz) weitergeführt. Um die Sensitivität auf d_n zu steigern, wird u.a. angestrebt, eine UCN-Speicherkammer aus einem neuartigen Material zu konstruieren. Eine Sitall-Glaskeramik soll dabei eingesetzt werden, die aufgrund ihrer Materialbeschaffenheit UCN mit hoher kinetischer Energie speichern kann, zugleich auch den Einsatz eines hohen elektrischen Feldes zwischen den die Speicherkammer begrenzenden Elektroden ermöglicht. Die Sensitivität der Messung ist proportional [2] zu:

$$\sigma_{dn} \propto \frac{1}{ET\sqrt{N}},$$

wobei E die elektrische Feldstärke, T die Messdauer und N die Anzahl der gespeicherten Neutronen angibt. Eine neue Speicherkammer kann gleichermaßen zu einer Erhöhung von N , E und T führen. Ergebnisse erster UCN-Speichermessungen werden im Folgenden präsentiert.

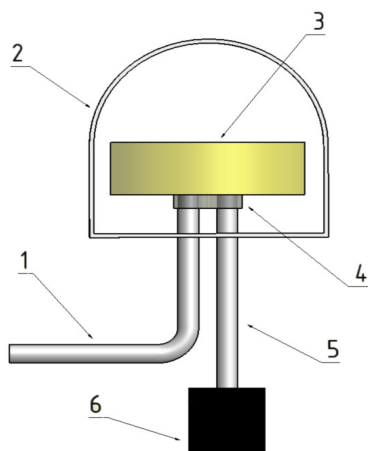


Abbildung 1. Aufbau des Experiments: (1) Strahlrohr von UCN-Quelle, (2) Vakuummutter, (3) Speicherkammer (Sitall), (4) UCN-Verschluss (Shutter), (5) Strahlrohr zum Detektor, (6) UCN-Detektor.

Experimentelles: Abb. 1 zeigt eine schematische Darstellung des Versuchsaufbaus. Die zylindrische Speicherkammer aus Sitall hat ein Volumen von etwa 20 Litern. Im Pulsbetrieb des Mainzer TRIGA Mark II Reaktors wird die Speicherkammer mit UCN aus der Quelle am Strahlrohr C gefüllt; 3 Sekunden nach dem Puls schließt ein Shutter die Kammer. Nach einer definierten Speicherzeit werden die „überlebenden“ UCN im Detektor nachgewiesen. Wir erhalten einen exponentiellen Abfall über die Speicherzeit (vgl. Abb. 2). Die effektive Speicherzeit τ_{eff} lässt sich aus der reziproken Summe der Lebensdauer des freien Neutrons τ_β , der Verluste durch Schlitze τ_{slit} und der Verluste durch Absorption ableiten.

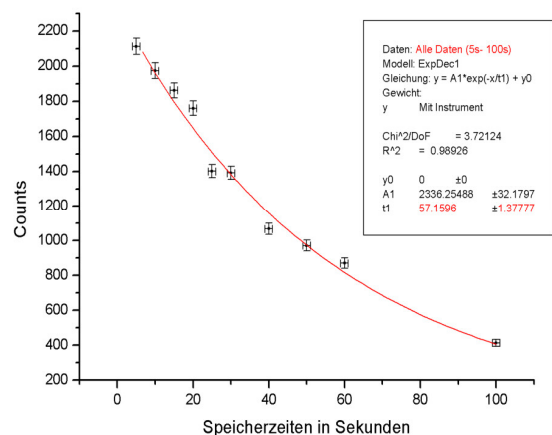


Abbildung 2. Die integrale Zählrate, aufgetragen gegen die Speicherzeit. Der exponentielle Fit ergibt eine Abfallkonstante von (57.2 ± 1.4) s.

Ergebnis: Mit der Messung einer Abfallkonstante von etwa 60 s und unter Einbeziehung der Verluste durch Schlitze erhält man eine untere Abschätzung von $\tau_{\text{eff}} \sim 100$ s. Sitall hat damit eine ähnliche Speichergüte wie andere in UCN-Experimenten eingesetzte Materialien. Es weist darüber hinaus einen hohen elektrischen Widerstand von $10^{16} \Omega \cdot \text{cm}$ auf und ist damit sehr hochspannungsfest. Weitere Messungen z.B. zur Depolarisationseigenschaft der UCN werden zeigen, ob das Material geeignet ist, in einem Experiment zur Messung des elektrischen Dipolmoments des Neutrons eingesetzt zu werden.

Referenzen:

- [1] A.D. Sakharov, Violation of CP invariance, C asymmetry and Baryon asymmetry of the Universe, JETP Lett. 5(32) 1967
- [2] P.G. Harris et al., New experimental limits on the Electric Dipole Moment of the Neutron, Physical Review Letter 82 ,5, 1998

Analyse von Fensterfolien für Ultrakalte Neutronen

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Einleitung

Am Schweizer Paul Scherrer Institut ist derzeit eine intensive Quelle für Ultrakalte Neutronen (UCN) im Aufbau [1]. Neutronen bezeichnet man als ultrakalt, wenn ihre Energie kleiner als etwa 250 neV ist. Solche Neutronen kann man in speziell beschichteten Behältern oder magnetischen Fallen speichern. Dies ermöglicht sehr präzise Messungen der fundamentalen Eigenschaften des freien Neutrons. Von besonderem Interesse sind dabei die genaue Bestimmung der Lebensdauer und die Suche nach einem elektrischen Dipolmoment des Neutrons.

Bei dieser UCN Quelle werden die Neutronen durch Spallation erzeugt und dann in schwerem Wasser (4 m³) zunächst auf thermische Energien moderiert. Die Konversion in den ultrakalten Energiebereich erfolgt durch inelastische Streuung an festem Deuterium (sD₂). Die UCN, die das Deuterium mit einer Energie von etwa 100 neV verlassen, werden über speziell beschichtete Rohre zu den Experimenten geleitet. Aus Sicherheitsgründen muss der Behälter mit 30 l sD₂ gegenüber den evakuierten Neutronenleitern abgeschlossen sein. Dies erfordert ein Material, das einerseits die UCN möglichst verlustfrei durchdringen können, das aber andererseits eine hohe mechanische Stabilität aufweist. Die Transmissionseigenschaften für UCN hängen vom Fermipotential und vom Absorptionsquerschnitt eines Materials ab. Das Fermipotential bestimmt die Reflektion von UCN an dem Material und sollte möglichst niedrig im Vergleich zur UCN Energie sein.

Unter diesen Gesichtspunkten sind Fenster aus reinem Aluminium oder Aluminium Legierungen (AlMg3) sowie aus Zirkon oder Zirkalloy besonders vielversprechend. In der Praxis jedoch können auch geringe Verunreinigungen insbesondere durch Elemente mit einem großen Neutroneneinfangquerschnitt die Transmissionseigenschaften erheblich beeinflussen. Aus diesem Grund wurden verschiedene Materialien mit der INAA am TRIGA Mainz und ergänzend mit ICP-MS, ICP-OES und GF-AAS an der TU Graz analysiert.

Proben

Insgesamt wurden 9 verschiedene Materialien analysiert, davon 3 aus reinem Al, 2 aus AlMg3, 2 aus reinem Zr und 2 aus Zirkalloy (Zr110 und Zr125).

Qualitative und quantitative INAA

Für eine erste qualitative Analyse wurden die Zirkon - Proben über die Rohrpost ($\Phi_{\text{therm}}=1,7 \cdot 10^{12} \text{ n/cm}^2 \text{ s}$) 1 Minute und 5 Minuten und im Karussell ($\Phi_{\text{therm}}=7 \cdot 10^{11} \text{ n/cm}^2 \text{ s}$) 60 Minuten bestrahlt. Längere Bestrahlungszeiten wären wegen der Aktivierung des Zirkons nicht sinnvoll. Bei den Aluminium - Proben wären hingegen wegen der kurzlebigen ²⁸Al-Aktivität Kurzzeitbestrahlungen nicht sinnvoll. Diese Proben wurden für 1 Stunde und 6 Stunden im Karussell bestrahlt. Bei den Zr - Proben konnten dabei je nach Material 10 bis 13 Elemente

sicher nachgewiesen werden, darunter: Co, Hf, In und Mn, die alle einen Neutroneneinfangquerschnitt $\sigma_{\text{nabs}} > 10$ barn aufweisen. In den Al - Proben wurden abhängig vom Material zwischen 11 und 20 Elementen sicher nachgewiesen. Elemente mit $\sigma_{\text{nabs}} \approx 10$ barn waren hier: Co, Hf, In, Mn und La.

Für die quantitative Analyse wurden die Zr - Proben 1 h, die Al - Proben 1 h, 6 h und 10 h bei $7 \cdot 10^{11} \text{ n/cm}^2 \text{ s}$ zusammen mit Referenz - Standards bestrahlt. Dabei konnten in den Zr Materialien die Gehalte bzw. Nachweisgrenzen für die Elemente Cr, Fe, In, Hf, Mn, Ta, und Zn bestimmt werden. Die quantitative Analyse der Al Materialien bezog sich auf die Elemente Cr, Co, Fe, Ga, In, Hf, La, Mn, Ni, Sb, Sc, U, und Zn.

ICPMS und ICPOES

Da die Gehalte der starken Neutronenabsorber B (768 barn) und Cd (242 barn) mit der INAA nicht bestimmt werden können, wurden an denselben Materialien ergänzend Analysen mit ICP-MS, ICP-OES und GF-AAS durchgeführt. Zusätzlich wurden dabei auch viele der Elementgehalte mitbestimmt, die bereits mit der INAA gemessen worden waren, um etwaige Fehlerquellen und Interferenzen der verschiedenen analytischen Verfahren zu erkennen. Viele Gehalte konnten so mit bis zu 3 unterschiedlichen Methoden bestätigt werden.

Ergebnisse

Die Tabelle 1 zeigt exemplarisch für die Mn - Gehalte einiger der untersuchten Materialien die wesentlichen Ergebnisse der Analyse. Zunächst einmal stimmen die Ergebnisse der verschiedenen Verfahren gut miteinander überein. Die gemessenen Gehalte variieren über mehrere Größenordnungen, sind jedoch für alle untersuchten Elemente klein, d.h. der Neutronenabsorptionsquerschnitt der untersuchten Materialien wird durch die gefundenen Verunreinigungen nur unwesentlich erhöht. Auf Grund dieser Analysen sind daher alle Materialien für den Einsatz als UCN Fenster gleichermaßen geeignet.

Mn [g/g]	Zr (1)	Zr 110	Al (1)	AlMg3
INAA	$3,08 \cdot 10^{-6}$	$5,5 \cdot 910^{-7}$	$3,16 \cdot 10^{-5}$	$2,97 \cdot 10^{-3}$
ICP-MS	$3,01 \cdot 10^{-6}$	$8,53 \cdot 10^{-7}$	$3,07 \cdot 10^{-5}$	$5,31 \cdot 10^{-3}$
ICP-OES			$2,41 \cdot 10^{-5}$	$2,80 \cdot 10^{-3}$

Tabelle 1: Vergleich der Mn Gehalte [g/g] aus INAA, ICP-MS und ICP-OES Messungen für einige der untersuchten Materialien

[1] <http://ucn.web.psi.ch/>

TRIGA-TRAP: A new facility for high-precision mass measurements on neutron-rich fission products and actinoids

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Introduction: The nuclear mass is one of the most fundamental properties in nature since it reflects all interactions in the nucleus. Therefore, high-precision mass data has its application in many fields of physics, but especially in nuclear astrophysics and nuclear structure studies [1]. The natural abundances of the elements as we observe today can be explained by different nucleosynthesis processes. One of them is the rapid neutron capture process (r-process), which proceeds far away from the stable nuclides in the region of nuclei with neutron excess. Most of them are presently not accessible in experiments, which has triggered the planning of new radioactive beam facilities. The research reactor TRIGA Mainz with the recently installed Penning trap mass spectrometer TRIGA-TRAP [2] already now provides the possibility to extend the limit for high-precision mass measurements towards the r-process nuclides. In off-line experiments samples of actinoids from uranium to californium will be investigated as well. Recently, the masses of the three nobelium isotopes ²⁵²⁻²⁵⁴No have been measured at SHIPTRAP (GSI, Darmstadt). Masses of other nuclides above uranium are determined via alpha-decay chains but have not been measured directly. TRIGA-TRAP is besides SHIPTRAP (GSI, Darmstadt) the only facility world-wide, where direct mass measurements of transuranium elements are performed.

Status of the experiment: After initial development at the physics institute, the TRIGA-TRAP mass spectrometer has been relocated and commissioned at beam port B of the TRIGA Mainz. The cryogenic double-Penning trap system has been very precisely positioned in a 7 T superconducting magnet. Two off-line ion sources were brought into operation, which provide stable reference ions like alkalines or carbon clusters [3]. Certain actinoids can be ionized as well by one of these sources. The carbon cluster ions are used for absolute mass calibration, and to perform systematic tests of the Penning trap setup. First measurements have been carried out in the second half of 2008, where cyclotron resonances have been recorded for different cluster sizes up to C₂₄⁺ (see Fig 1). Due to comparably high residual gas pressure in the measurement trap, the excitation time, and thus, the line width of the resonance presently limit the achievable relative mass uncertainty to about 10⁻⁷ using a conventional non-interrupted excitation scheme. By the implementation of time-separated oscillatory fields, which is known as the Ramsey technique [4], the uncertainty could be improved to about 5×10⁻⁸ for a single measurement sufficient for first mass measurements on actinoid elements. The feasibility of this approach has been demonstrated by performing measurements on several gadolinium isotopes and first data on ²⁴¹Am¹⁶O⁺ ions have been recorded.

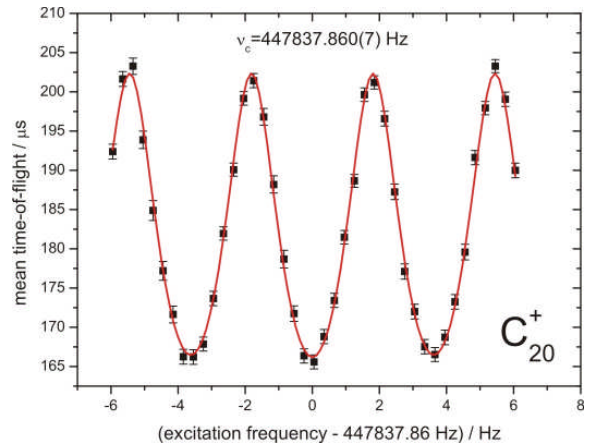


Figure 1. Excitation of C₂₀⁺ carbon cluster ions with time-separated oscillatory fields including a fit of the theoretical line shape. The mass value is extracted from the centroid frequency.

Outlook: A new differential pumping-barrier assembly will be implemented in order to suppress the helium buffer gas flow between the preparation trap and measurement trap further. In addition, an ion getter pump will be installed. These improvements will enable extended observation times, thus line widths below 1 Hz could be achieved. Extensive work is undertaken to set-up an ECR source on a high-voltage platform in combination with a carbon aerosol gas jet arrangement in order to have access to fission products from the reactor [5].

We will focus on finalizing and commissioning the non-destructive ion detection system. Having two independent ion detection techniques implemented within the same Penning trap mass spectrometer, TRIGA-TRAP will be unique among the on-line Penning trap mass spectrometers for short-lived nuclides. Ultimately single-ion sensitivity will enable measurements on nuclides with extremely low production rate [6].

References

- [1] K. Blaum, Phys. Rep. 425 (2006) 1-78.
- [2] J. Ketelaer et al., Nucl. Instr. Meth. A 594 (2008) 162-177.
- [3] C. Smorra et al., this issue.
- [4] S. George et al., Phys. Rev. Lett. 98 (2007) 162501.
- [5] M. Eibach et al., this issue.
- [6] J. Ketelaer et al., Eur. Phys. J. A, accepted (2008).

Acknowledgement

Financial support is acknowledged from the Helmholtz Association for National Research Centers (HGF) under contracts VH-NG-037 and VH-NG-148 as well as by the Stiftung Rheinland-Pfalz für Innovation under contract 854. Sz. Nagy acknowledges the support of the Alliance Program of the Helmholtz Association. We also thank P. Thörle-Pospiech and the technical staff of the TRIGA Mainz reactor. D. Beck from GSI/Darmstadt and the CS development team are acknowledged for their support.

A carbon cluster ion source for absolute mass calibration at TRIGA-TRAP

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Introduction and motivation: Penning trap mass spectrometers are leading devices to determine one of the most fundamental property of a nucleus: its mass [1]. To this end, the cyclotron frequency $\nu_c = qB / (2\pi m)$ of a stored ion is measured, where q denotes the charge, m the mass of the ion, and B the magnetic field strength, which is obtained from a calibration with a reference ion of well-known mass. A new laser ablation ion source was developed for TRIGA-TRAP [2] to produce carbon cluster reference ions, facilitating absolute mass measurements, since carbon clusters are integer multiples of the atomic mass unit. Systematic studies of the accuracy of the mass spectrometer can be performed by carbon cluster cross-reference measurements [3], in which the well known frequency ratio of two different carbon cluster ions is determined. Furthermore, since a large variety of reference ions with well-known mass is provided, a reference ion species with a cyclotron frequency similar to the ion of interest can be selected in order to minimize systematic mass dependent uncertainties.

Experimental setup and results: Laser ablation is the common approach to generate carbon clusters for mass spectrometry purposes. At TRIGA-TRAP a pulse from a frequency-doubled Continuum Minilite Nd:YAG laser at a wavelength of $\lambda = 532$ nm, with a pulse width of $\tau = 5$ ns, and a repetition rate below 1 Hz is guided into a vacuum chamber and focussed on a Sigradur[®] target with an energy density of 120 to 250 MW/cm². Thereby, carbon is removed from the target surface, and a plasma is formed, in which carbon clusters are created and ionized. Afterwards, they are extracted by an electrode of Pierce geometry, focussed by an Einzel lens and after a 90° deflection guided by conventional ion optics into the Penning traps. A detailed description of the ion source is found in [4, 5].

The laser ablation ion source produces an ion pulse composed of a mixture of ions of a broad mass range. In order to analyse the mass spectrum, the ions were stored in a Penning trap, where their initial energy spread is reduced by collisions with helium buffer gas. Subsequently, the cooled ions are ejected from the trap and detected with a channeltron-type electron multiplier detector. Ions of different masses are distinguished by their time of flight, as shown in figure 1. Clusters up to C₂₄⁺ (mass 288 u) were successfully produced, thus the entire nuclide chart can be covered with reference ions. The desired cluster species is selected by applying a mass selective buffer-gas cooling technique in the preparation trap, so that a clean ion bunch is available for the actual measurement in the precision trap.

The same source has been used to produce a sufficient amount of gadolinium monoxide ions and americium monoxide ions for a first off-line mass measurement.

Conclusion and outlook: A laser ablation ion source for the production of carbon cluster ions was developed, tested and brought into operation at the TRIGA-TRAP facility. Reference ions for absolute mass calibration are thus available, and the stability of the source was demonstrated by 14 hours continuous operation without any maintenance. Mass measurements on lanthanoide and actinoide elements are currently in progress.

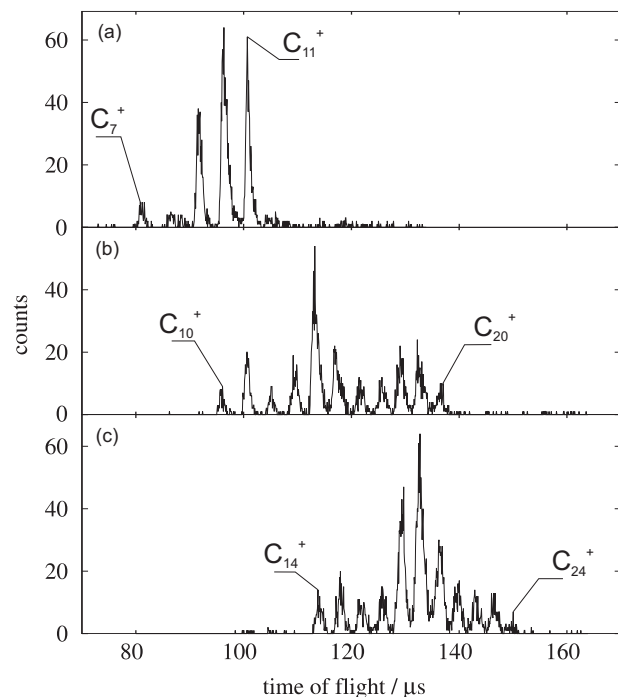


Figure 1. Time-of-flight spectra recorded after ejection of carbon clusters from the preparation Penning trap in order to identify the ion species. Different fractions of the mass spectrum produced by the ion source were sampled.

References

- [1] Blaum K. Phys. Rep. 425 1-78, 2006.
- [2] Ketelaer J. *et al.* Nucl. Instrum. Meth. A 594 162-177, 2008.
- [3] Kellerbauer A. *et al.* Int. J. Mass Spectr. 229 107-115, 2003.
- [4] Smorra C. Diploma thesis, Johannes Gutenberg-Universität Mainz, 2008.
- [5] Smorra C. *et al.*, submitted to J. Phys. B (2009)

Acknowledgements

Financial support is acknowledged from the Helmholtz Association for National Research Centers (HGF) under Contract VH-NG-037 and VH-NG-148 as well as by the Stiftung Rheinland-Pfalz für Innovation under Contract 854. Sz. Nagy acknowledges the support of the Alliance Program of the Helmholtz Association. We also thank P. Thörle-Pospiech and the technical staff of the TRIGA Mainz reactor. D. Beck and F. Herfurth from GSI/Darmstadt, and the CS development team are acknowledged for their support.

Extraction of fission products for TRIGA-SPEC using a helium gas jet with carbon aerosols

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Introduction: High-precision measurements of nuclear ground-state properties like masses, magnetic moments, spin and charge radii reflect the interactions inside the nucleus and are therefore of fundamental importance, with applications in nuclear structure and nucleosynthesis studies [1]. The TRIGA-SPEC experiment at the TRIGA Mainz reactor aims to investigate neutron-rich fission products and determine these properties in a model independent way by means of Penning trap mass spectrometry and laser spectroscopy [2]. A helium gas-jet arrangement in combination with a carbon aerosol generator has been implemented in order to transfer neutron-rich fission products from the reactor to the TRIGA-SPEC experiment. The gas-jet arrangement will be connected to a 30 cm³ target chamber close to the reactor core containing a fissionable target, e.g. ²³⁵U or ²⁴⁹Cf. The thermal neutron induced fission products having energies of approximately 100 MeV thermalize in the helium gas at a pressure of about 2.5 bars. After thermalization they attach to the carbon aerosols that are added to the gas and can be flushed out of the target chamber in a laminar flow through a PE-capillary to a skimmer system where the helium gas is separated from the aerosols. In order to release the fission products from the aerosols and to ionize them, an ECR ion source is being installed on a high-voltage platform. After ionization the fission products will be mass separated in a 90° dipole magnet and finally transferred either towards the laser spectroscopy experiment or the Penning trap mass spectrometer [3].

Experimental setup and results: Carbon aerosols are produced by constantly charging a capacitor between two sharpened pure graphite electrodes placed in a helium gas flow. When the breakdown voltage of about 1.5 kV is reached, a spark discharge takes place and carbon evaporates. The repetition rate of the discharge can be easily adjusted through the charging current. Using an electrostatic classifier we observed that the carbon vapour condenses to particles with a diameter of 10 nm to 1 μm lognormally distributed around a maximum at about 100 nm at a gas flow of 1.4 l/min. Despite the erosion of the electrodes, the continuous production of aerosols has been demonstrated over about 8 hours without maintenance, satisfying the requirements of the TRIGA-SPEC experiments. The accessibility of radionuclides away from the valley of β-stability depends on their half-lives and production rates, thus a rapid and efficient transfer to the experiment is crucial. Thermalization in the target chamber and the transport to the ion source defines mainly the total transfer time since the ionization and the transport of ions are very fast. Hence, the transport time of the fission products has been determined by guiding the

aerosols through a 7 m long capillary of 0.86 mm diameter to a filter placed in front of a γ-detector during a reactor pulse. As shown in Fig. 1 γ-radiation is emitted during the reactor pulse, which is observed by the detector. The peak shape as well as the neutron flux in the reactor can be approximated with a Gaussian distribution. After a few hundred milliseconds the fission products arrive and the activity increases first to a maximum and decreases afterwards again down to background level. The transport time is defined as the time difference between the maximum of the reactor pulse and the half of the maximum of the activity that is caused by the arriving fission products and is determined to be about 400 ms.

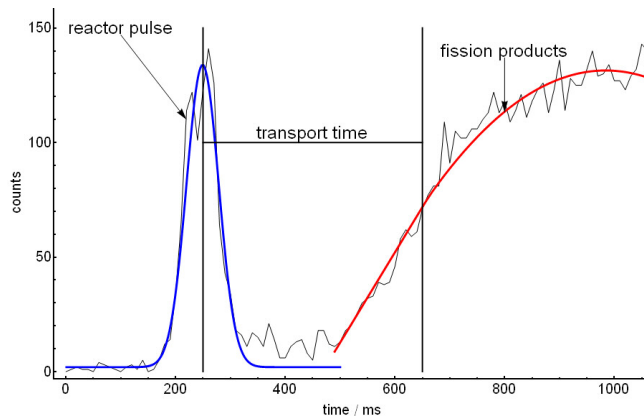


Figure 1: γ-activity recorded during and after a reactor pulse. The transport time is defined as the time difference between the maximum of the pulse and the half of the maximum activity that is caused by the arriving fission products.

Conclusions and outlook:

The extraction of fission products using carbon aerosols was demonstrated. The transport efficiency will be investigated in detail. Values up to 70% have been reached in first tests.

Next steps are to finalize the ECR ion source and connect it to the gas jet via a skimmer to study the ion production.

References:

- [1] K. Blaum, Phys. Rep. 425 (2006) 1-78.
- [2] J. Ketelaer et al., Nucl. Instr. Meth. A 594 (2008) 162-177.
- [3] see reports to TRIGA-LASER and TRIGA-TRAP in this issue

Acknowledgement:

Financial support is acknowledged from the Helmholtz Association for National Research Centers (HGF) under contracts VH-NG-037 and VH-NG-148 as well as by the Stiftung Rheinland-Pfalz für Innovation under contract 854. Sz. Nagy acknowledges the support of the Alliance Program of the Helmholtz Association. We also thank the technical staff of the TRIGA Mainz reactor.

TRIGA-LASER: A collinear laser spectroscopy beamline at the TRIGA reactor Mainz

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Introduction: Collinear Laser spectroscopy of radioactive nuclei can provide fundamental information on the structure of radioactive nuclei. The dependencies of the hyperfine splitting and isotope shift on the nuclear moments and mean square nuclear charge radii are well known and the theoretical framework for the extraction of nuclear parameters is well established. We have started to set up the *TRIGA-LASER* experiment at the University Mainz. It will allow us to perform new measurements on neutron rich isotopes produced at the research reactor [1], but it will also serve as a development platform for the *LaSpec* experiment [2] at *FAIR*, *GSI*.

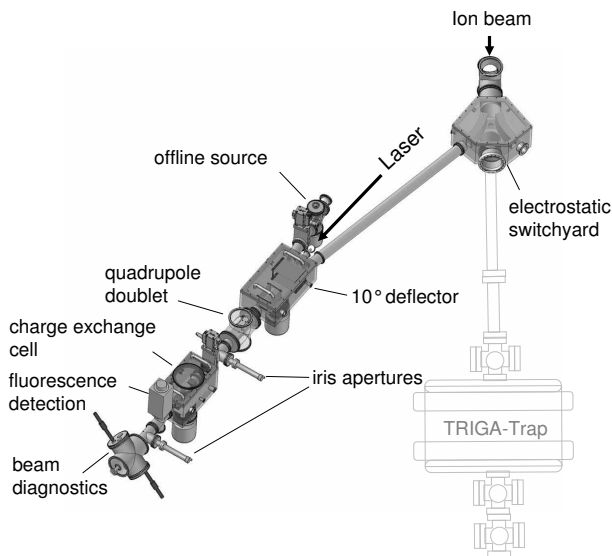


Figure 1: Drawing of the collinear beamline. All components except the switchyard and the detection unit are already installed.

Experimental: The vacuum system of the laser beamline was assembled after machining of the electrostatic deflection chamber and the chamber for the charge exchange cell according to our custom design. A vacuum pressure of 2×10^{-7} mbar could be reached without baking. In Fig. 1 a drawing of the complete laser beamline is shown. For commissioning purposes, an offline surface ion source based on an electro-thermally heated graphite oven was constructed. The source is operated in a HV cage and can be set to voltages up to 10 kV. For fast loading of the ionizer tube, the source chamber is separated from the laser vacuum sys-

tem with a valve and can be pumped with a separate turbo molecular pump.

Results: First tests showed 70% ion beam transmission with 3.5 nA current on the Faraday cup after the non-operating charge exchange cell. For ion beam profile monitoring a fork scanner system 5100 from Danfysik was installed to get a good control of the ion beam diameter, which is essential for a good overlap between the laser and ion beam. In Fig. 2 a plot of the beam profile at the end of the ion beamline in both, horizontal and vertical plane is shown.

First laser spectroscopy test measurements will be performed with Rb atoms after charge exchange. The transition at 780 nm wavelength can be excited with a diode laser which will be frequency locked to a HighFinesse WS7 wavemeter. This allows to install a compact laser system next to the beamline.

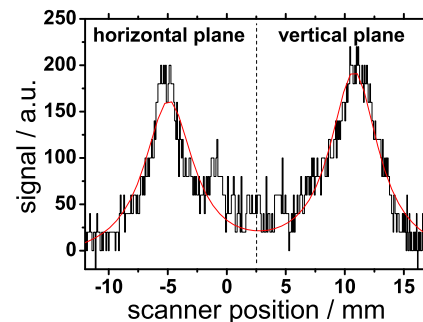


Figure 2: Beam profile of a 300 pA Li^+ beam at 2 keV energy in horizontal and vertical plane. The corresponding beam diameter was estimated to be 5 mm.

Acknowledgement

Work supported by HGF under contract VH-NG-148 and 'Stiftung Rheinland-Pfalz für Innovation' under contract 854.

References

- [1] J. Ketelaer, J. Krämer, et al., Nucl. Instrum. Methods Phys. Res., Sect. A **594** (2008) 162-177.
- [2] W. Nörtershäuser, P. Campbell, and the LaSpec collaboration, Hyp. Int. **171** (2006) 149.

A Solid State Laser System for the Cooling of Magnesium Ions

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Introduction: Sympathetic cooling of ions in Paul and Penning traps would be advantageous for proposed experiments at the TRIGA reactor Mainz as well as at GSI Darmstadt. Magnesium ions are favourable for such a cooling scheme since they have a closed two-level system and lasers for repumping are not required. However, light at the transition wavelength of 279.5 nm has to be produced either by frequency doubling of a dye laser or frequency quadrupling of a fiber laser. We have chosen the solid state approach and the system will later be composed of a 1.5 W fiber laser at 1118 nm and two second harmonic generation (SHG) cavities for frequency quadrupling. Currently we are setting up the first doubling-stage for a fiber laser and we will later apply the system at the TRIGA-SPEC as well as on the SPECTRAP setup at GSI.

Experimental: We used a Koheras Boostik fiber laser as the fundamental laser source for the first SHG cavity. The laser has 1.5 W maximum output power, less than 70 kHz linewidth and a very good beam quality: M^2 less than 1.05. The output polarization can be optimized and controlled with a quarter- and a half-waveplate. An optical isolator is used for avoiding back reflections in the laser (figure 1).

For the first SHG cavity we used a LBO nonlinear crystal because of its high damage threshold and the possibility to use the more efficient non-critical phase matching (NCPM) at 89°C, type I XY/XZ, $\theta=90^\circ$, $\varphi=0^\circ$ [1].

Using the Boyd Kleinman [2] theory and evaluating the optimizable parameters, we came to an optimum length of 20 mm for the crystal. Considering that we use NCPM and the walk-off angle between fundamental and second harmonic light is 0° , the optimum focus inside the crystal with this length is for a beam waist of 28 μm . For the cavity we had to estimate all losses of the fundamental laser light: from doubling, surface reflections and due to the absorption inside the crystal. Therefore, we chose a 97.5% reflectivity at 1118 nm of the input mirror M1 for impedance matching. This corresponds to a cavity enhancement factor of 40.

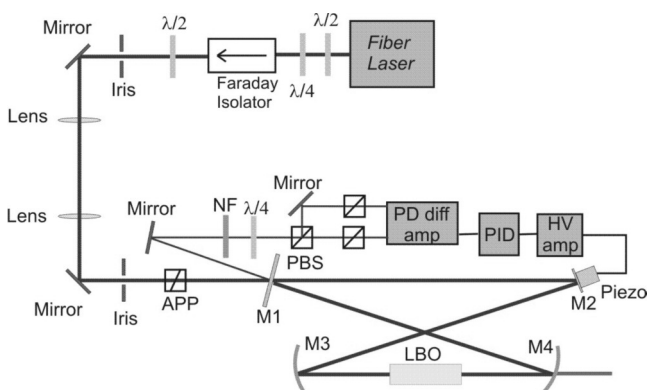


Figure 1. Setup of the Laser and the first SHG cavity.

Using the ray transfer matrix analysis [3] we designed a bow tie resonator that allows us to fit the oven with the crystal in the middle of the short arm and to obtain a 28 μm beam waist in the middle of the crystal (see Fig. 2).

M1 is AR coated for 1118 nm on the outside relative to the cavity. M2 is highly reflective (>99.9%) for 1118 nm and is mounted on a piezo mirror shifter for fine adjustments of the cavity length. For the focusing arm we used two plano-concave mirrors with $f=70$ mm and with a distance between of $d=154$ mm. M3 is highly reflective (>99.9%) for 1118 nm while the output coupler is highly reflective (>99.8%) for 1118 and transmissive ($T>94\%$) for the second harmonic wavelength of 559 nm.

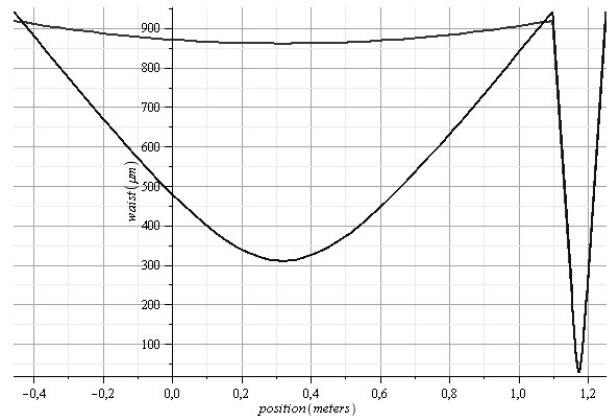


Figure 2. Beam waist size inside the cavity for the sagittal and tangential plane.

The total length of the cavity is 1709 mm and has a full folding angle of 30° . Because of this big folding angle we obtained an astigmatic focus in the middle of the long arm and we had to use an anamorphic prism pair besides two convex lenses in order to obtain a proper mode matching. For locking the cavity we used the Hänsch-Couillaud polarisation analysis locking scheme [4].

Results: We obtained up to 75% coupling efficiency of the fundamental beam into the cavity. Locking was stable for power inputs up to ~ 500 mW. The maximum green output was approximately 50 mW for 950 mW fundamental power at the input.

Further efforts must be made in order to increase the efficiency of the doubling by better alignment and reduction of losses and for increasing the locking stability at higher power levels.

References

- [1] A. Friederauer, F. Markert, Appl. Phys. B **84**, 371 (2006).
- [2] G.D. Boyd, D.A. Kleinman, J. Appl. Phys. **39**(8), 3597(1968).
- [3] T. Freearge, C. Zimmermann, Opt. Comm. **199**, 435 (2001).
- [4] T.W. Hänsch, B. Couillaud, Opt. Commun. **35**, 441 (1980).

Acknowledgement

This work was supported by the Helmholtz Association under Contract VH-NG-148.

Charge radius determination of $^{7,9,10}\text{Be}$ and the one-neutron halo nucleus ^{11}Be by high-resolution collinear laser spectroscopy

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After successful studies of the charge radii along the isotopic chains of the light elements lithium [1] and helium [2] by means of high-resolution laser spectroscopy, the focus of the charge radii measurements of light elements is now directed towards beryllium isotopes, because ^{11}Be is a one-neutron halo nucleus and ^{14}Be is a two or four neutron halo isotope.

We have previously proposed measurements of Be on trapped and cooled ions in a linear Paul trap [3,4] but have now found an alternative approach. The spectroscopy of the stable and radioactive beryllium ions was performed by collinear spectroscopy on a 60 keV ion beam. This appeared possible since first theoretical calculations [5,6] consistently predicted a field shift coefficient of about -17 MHz/fm^2 , which means that the remaining s electron is 10 times more sensitive on the proton distribution than in the case of Li or He. Hence the accuracy needed in the determination of the isotope shift is on the order of 2 MHz. This can be reached by simultaneous collinear/ anti-collinear laser spectroscopy at the existing COLLAPS beamline at ISOLDE, CERN [8]. For this approach a frequency-comb-based laser locking scheme was developed and allowed the determination of the absolute transition frequencies in the D1 and D2 line for $^{7,9,10,11}\text{Be}^+$ ions.

A preceding series of measurements on $^9\text{Be}^+$ indicated that systematic errors are sufficiently small to reach the required accuracy. The main contribution is the laser beam alignment with 500 kHz and 400 kHz uncertainty introduced by the rubidium clock, which was used as a reference in the laser locking scheme.

With the determined isotope shift and high precision calculations of the mass-shift contribution it is possible to extract the charge radius for $^{7,10,11}\text{Be}$ based on the previous known value of ^9Be [9]. The development of charge radii along the isotopic chain is shown in Fig. 1 (solid circles). The theoretical models shown for comparison are the no-core-shell model (NCSM) [10], fermionic molecular dynamic (FMD) [10] and Greens function Monte Carlo calculations (GFMC) [12]. They all describe the observed trend of charge radii very well. Radii extracted with a Glauber model from interaction cross sections (open circles) [13] strongly overestimate the charge radius of ^{11}Be , which emphasizes the necessity for model-independent experimental approaches.

Acknowledgement: this work is supported by BMBF Contract Nos. 06TU263I, 06UL264I, and 06MZ215/TP6, Helmholtz Association Contract VH-ANG-148 and the EU (FP-6 EU RII3-CT-2004-506065)

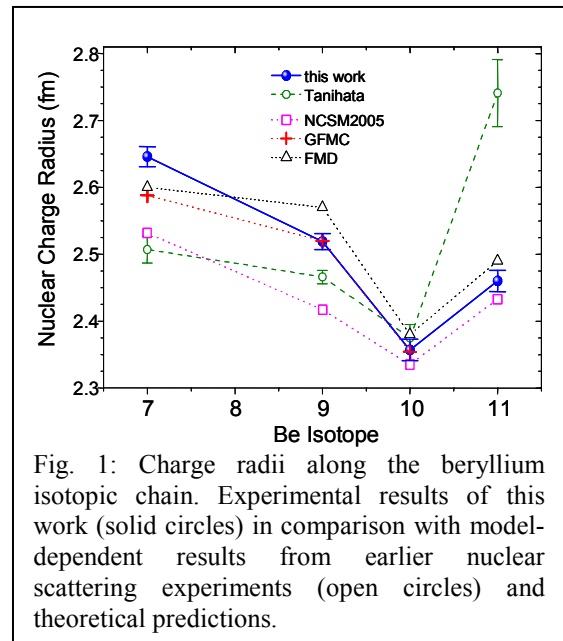


Fig. 1: Charge radii along the beryllium isotopic chain. Experimental results of this work (solid circles) in comparison with model-dependent results from earlier nuclear scattering experiments (open circles) and theoretical predictions.

If one solely allocates the increase in charge radius from ^{10}Be to ^{11}Be to an increased center of mass motion of the ^{10}Be residual core a distance of the halo neutron to the center of mass of 7.0 fm is obtained.

From fitting the observed hyperfine structure of the odd isotopes it was possible to extract the A-factors in the 2s and 2p $_{1/2}$ state and therewith the magnetic moments as described in [8].

In the near future the investigation of ^{12}Be is planned for 2010 applying the ISCOOL cooler and buncher at ISOLDE. Test measurements at ISCOOL are already in progress.

References

- [1] R. Sanchez et al., PRL96, 033002 (2006)
- [2] P. Müller et al., PRL 99, 252501 (2007)
- [3] M. Zakova et al., Hyp. Int. 171, 189 (2006)
- [4] D. Tiedemann et al., GSI annual report, 266 (2006)
- [5] Z.-C. Yan et al., PRL 100, 243002 (2008)
- [6] K. Pachucki et al., Phys Rev A 78,052511 (2008)
- [7] G. Borghs et al., Optics Comm. 38, 101 (1985)
- [8] W. Nörtershäuser et al., PRL Vol. 102 (2009) in print
- [9] J.A. Jansen et al., Nucl. Phys.A 188, 337 (1972).
- [10] C. Forssen, Phys. Rev. C71, 044312 (2005) and priv. comm.
- [11] R. Torabi, priv. comm. (2008)
- [12] S. Pieper, PRC 66, 044310 (2002)
- [13] I. Tanihata, Phys. Lett. B 206, 592 (1988)
- [14] W. M. Itano, Phys. Rev. B 27, 1906 (1983).

TASCA Commissioning Completed*

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The TransActinide Separator and Chemistry Apparatus (TASCA) project [1], which is focusing on the separation and investigation of neutron-rich transactinide nuclides produced in actinide-target based reactions, has successfully finished its commissioning; see [2] for an interim report. TASCA is ready for the envisioned research program which includes both chemical investigations of transactinide or superheavy elements (SHE) after pre-separation with the gas-filled separator and nuclear structure and nuclear reaction studies.

The central device of TASCA is a gas-filled separator in a DQQ configuration operated either in the "High Transmission Mode" (HTM, DQ_hQ_v) or in the "Small Image Mode" (SIM, DQ_vQ_h) [1-5]. In the HTM, the unsurpassed transmission of TASCA - at a relatively low dispersion - is exploited. In contrast, the SIM provides unique possibilities due to its small spot size in the focal plane (< 3 cm diam.) at a still relatively high transmission; see Table 1.

Table 1: Important parameters of TASCA, calculated for the reaction ⁴⁸Ca(²⁴⁴Pu,3n)²⁸⁹114, in comparison with other gas-filled separators operated in SHE research.

Separator	Con-figuration	Trans-mission %	Dis-persion mm/%	Bρ (max) Tm
DGFRS	DQ _h Q _v	35	7.5	3.1
GARIS	DQ _h Q _v D	40	9.7	2.16
BGS	Q _v D _h D	49-59	20	2.5
TASCA	DQ _h Q _v	60	9	2.3
TASCA	DQ _v Q _h	35	1	2.3

Table 2 provides a compilation of all nuclear reactions and reaction products applied and detected in the course of the commissioning program together with the mode TASCA was operated in and the fill gas. Also listed are experiments to test and optimize the recoil transfer chambers (RTC) [6], the gas-jet transport of pre-separated products into our Rotating wheel On-line Multidetector Analyzer (ROMA), and its performance, and the coupling and

use of aqueous chemistry set-ups behind TASCA.

Table 2: Nuclear reactions and their products used to commission TASCA; H=HTM, S=SIM, TSp=TASISpec, R=ROMA, C=chemistry, catch=catcher foils.

Product	xn	Beam	Target	Mode	Gas	RTC +R/C
³⁰ Si	--	³⁰ Si	--	H,S	Vac	
^{173,175} Os	7n	⁴⁰ Ar	^{nat} Ce	H	He	C
¹⁸⁰⁻¹⁸² Hg	2-4n	⁴⁰ Ar	¹⁴⁴ Sm	H,S	He	C
¹⁸⁸ Pb	4n	⁴⁸ Ca	¹⁴⁴ Sm	H,S	He	
¹⁸⁸ Pb	4n	⁴⁰ Ar	¹⁵² Gd	H,S	He	
¹⁹⁴⁻¹⁹⁶ Pb	4-5n	⁴⁰ Ar	^{nat} Gd	H,S	He	R
¹⁹⁸⁻¹⁹⁹ Bi	4-5n	²² Ne	¹⁸¹ Ta	H,S	He	catch
¹⁹⁵⁻¹⁹⁶ Po	4-5n	⁴⁸ Ca	¹⁵² Gd,	H	He	R
²⁰⁰ At	3n	⁶⁴ Ni	^{nat} La	TSp	He	
²⁰⁰ Fr	5n	⁶⁴ Ni	¹⁴¹ Pr	TSp	He	
²⁰⁵⁻²⁰⁶ Fr	5-6n	³⁰ Si	¹⁸¹ Ta	H	He	
²⁰⁸⁻²¹¹ Ra	3-4n	⁵⁴ Cr	^{nat} Gd	H,S	He	
²⁰⁸⁻²¹¹ Ra	3-6n	⁶⁴ Ni	¹⁵⁰ Nd	TSp	He	
²¹⁰ Ac	5n	⁴⁰ Ar	^{nat} Lu	H,S	He,N ₂	
²¹⁵ Ac	4n	²² Ne	¹⁹⁷ Au	H,S	He,H ₂	
^{218-x} Th	xn	⁶⁴ Ni	¹⁵⁴ Sm	TSp	He	
^{224-x} U	xn	⁶⁴ Ni	^{nat} Gd	TSp	He,H ₂	
²⁴⁵ Fm	3n	⁴⁰ Ar	²⁰⁸ Pb	H,S	He	R
²⁵² No	2n	⁴⁸ Ca	²⁰⁶ Pb	H,S,	He	R
				TSp		
²⁵³ No	2n	⁴⁸ Ca	²⁰⁷ Pb	H,	He	
				TSp		
²⁵⁴ No	2n	⁴⁸ Ca	²⁰⁸ Pb	H,S	He,H ₂	
²⁵⁵ No	5n	²² Ne	²³⁸ U	H,S	He,H ₂	R
²⁵⁶ No	4n	²² Ne	²³⁸ U	H	He	
²⁶⁰ Rf	6n	²² Ne	²⁴⁴ Pu	H	He,H ₂	
^{261a,261b} Rf	5n	²² Ne	²⁴⁴ Pu	H	He	R,C
²⁶² Rf	4n	²² Ne	²⁴⁴ Pu	H	He,H ₂	

Extensive studies have been performed in the HTM and SIM to obtain optimized parameter sets for (i) the target thickness and stability, (ii) the gas pressure and the gas filling (He, H₂, and mixtures), (iii) the dipole setting (Bρ) and quadrupole focusing, (iv) the RTCs (window material and thickness, support structures, and size and shape of the chamber), (iv) gas-jet transport of pre-separated products, and (vi) the coupling and performance of devices

* Work supported by BMBF (06MT2471, 06MT248, 06MZ2231) and GSI-F&E (MT/TÜR, MZJVKR)

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like ROMA and the Automated Rapid Chemistry Apparatus (ARCA). Results of many of these parameter studies were compared with TASCAs model calculations [7] and very good agreement was achieved. This agreement is of special importance as it allows for the selection of proper settings for magnetic rigidities (Bp) in the dipole magnet and the quadrupole magnets for all nuclear reactions and for all gases and gas mixtures tested at various pressures. It is especially rewarding to see that not only Bp values were properly chosen to centre product distributions on focal plane detectors (FPD) but also that the measured spatial distributions and, more importantly, the efficiencies were in very good agreement with model calculations. These results confidently demonstrate that we are able to perform trustworthy SHE experiments with TASCAs. In the following, we mention a few concluding experiments, some of the highlights and new developments; see [2] for additional information on the parameter studies.

The first efficiency measurements with catcher foils behind the target and in the focal plane showed very good agreement with model calculations for the fairly asymmetric reaction $^{22}\text{Ne}(^{181}\text{Ta},\text{xn})^{198\text{m},199}\text{Bi}$ [2]. To confirm this agreement in a more symmetric reaction, leading to a significantly heavier reaction product, and to obtain a standard reaction to test and check the TASCAs performance, detailed studies were performed with well known reactions of ^{48}Ca with $\approx 0.5 \text{ mg/cm}^2$ thick targets of $^{206,207,208}\text{Pb}$ leading to $^{252,253,254}\text{No}$. Assuming cross sections of $0.5 \mu\text{b}$, $1.3 \mu\text{b}$, and $2 \mu\text{b}$ [8] for the production of ^{252}No , ^{253}No , and ^{254}No , efficiencies of 54%, 56%, and 50%, respectively, were obtained for the HTM, using a He filling of 0.8 mbar, and a (80x36) mm^2 16-strip FPD. Taking into account uncertainties in cross sections and systematic errors of target thicknesses and beam current measurements, we observe an excellent agreement with model calculations [7] predicting 54%. Equally good is the agreement in the SIM, at a He pressure of 0.8 mbar, where a 30% efficiency was measured for the reaction $^{48}\text{Ca}(^{208}\text{Pb},2\text{n})^{254}\text{No}$.

A new (140x40) mm^2 large, highly efficient FPD, consisting of double-sided silicon strip detectors (DSSSD) in the focal plane and SSSDs for the backward box detectors will further increase the TASCAs efficiency; see [9] for details of the new detector.

As one of the crucial tests and one of the highlights finalizing the TASCAs commissioning program, we studied the isotopes ^{260}Rf , $^{261\text{a},261\text{b}}\text{Rf}$, and ^{262}Rf synthesized in the very asymmetric reaction $^{22}\text{Ne} + ^{244}\text{Pu}$; see [10] for details of the nuclear reactions, for TASCAs parameters, and for the interesting nuclear decay results. In essence, the performance of TASCAs was as anticipated; everything worked well, including the ^{244}Pu target wheel. Efficiencies and magnetic settings (Bp=1.99 Tm at 0.4 mbar He, HTM) were as expected. As observed in previous experiments [2], it was again possible to reduce the background in the FPD by using a mixture of He and H_2 . This part of the commissioning program showed clearly that TASCAs can be applied efficiently for nuclear decay and nuclear

reaction studies of neutron-rich nuclides of SHE synthesized in very asymmetric hot-fusion reactions. Rf isotopes were not only measured in the FPD but were also collected in an RTC and were transported either to ROMA for nuclear decay measurements [10] or to ARCA for chemical investigations [11].

An additional highlight of the experiment was the first transactinide chemistry behind TASCAs designed as a proof-of-principle experiment. It was performed in ARCA with pre-separated 78-s $^{261\text{a}}\text{Rf}$; details of the nuclear reaction and the Rf separation in TASCAs are described in [10] while all chemical aspects are discussed in [11]. This successful experiment, which studied the formation of Rf-fluoride complexes and their adsorption behaviour on an anion-exchange resin, demonstrated that aqueous-phase transactinide chemistry behind TASCAs can now be performed.

The new set-up termed *TAsca Small Image mode Spectroscopy* (TASISpec) [12] exploits advantages of the SIM, i.e. the fact that neutron-rich nuclides of SHE, produced in hot-fusion reactions, can be focused with high efficiency into an area of $< 7 \text{ cm}^2$. This provides the unique possibility to build a compact Si-detector box for α -particle, electron, and fission-fragment measurements, and to pack composite Ge-detectors in very close geometry, resulting in an unprecedented, highly efficient set-up for multi-coincidence measurements with γ -rays and X-rays; see [12] for details. A prototype set-up has been commissioned successfully and first data have been collected for nuclides as heavy as $^{252,253}\text{No}$.

In conclusion, the performance of TASCAs as a separator is well understood and is perfectly under control. TASCAs as a whole is presently the most versatile and highest efficient instrument in SHE research worldwide. It has entered the region of transactinides or superheavy elements, and is ready to explore the physics and chemistry of the "terra incognita" it was designed and built for.

References

- [1] M. Schädel *et al.*, GSI Sci. Rep. 2005, GSI Report 2006-1, 2006, p. 262, and <http://www.gsi.de/TASCA>
- [2] M. Schädel *et al.*, GSI Sci. Rep. 2007, GSI Report 2008-1, 2008, p. 152.
- [3] M. Schädel, Eur. Phys. J. D 45 (2007) 67.
- [4] A. Semchenkov *et al.*, Nucl. Instr. and Meth. in Phys. Res. B 266 (2008) 4153.
- [5] Ch.E. Düllmann *et al.*, Nucl. Instr. and Meth. in Phys. Res. B 266 (2008) 4123.
- [6] Ch.E. Düllmann *et al.*, GSI Sci. Rep. 2006, GSI Report 2007-1, 2007, p. 146.
- [7] K.E. Gregorich *et al.*, GSI Sci. Rep. 2006, GSI Report 2007-1, 2007, p. 144.
- [8] Yu. Ts. Oganessian *et al.*, Phys. Rev. C 64 (2001) 054606.
- [9] A. Yakushev *et al.*, contribution to this report.
- [10] A. Gorshkov *et al.*, contribution to this report.
- [11] J. Even *et al.*, contribution to this report.
- [12] L.-L. Andersson *et al.*, contribution to this report.

First Transactinide Chemistry Behind TASCA*

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The final phase of the TASCA commissioning program [1] included a series of experiments with ²⁶⁰Rf, ^{261a,b}Rf and ²⁶²Rf produced in the ²⁴⁴Pu(²²Ne,xn) reaction. One of the highlights was a proof-of-principle transactinide chemistry experiment with 78-s ^{261a}Rf. The Automated Rapid Chemistry Apparatus (ARCA) [2] was used to study the formation of fluoride complexes of Rf in diluted HF-solution by anion-exchange chromatography.

TASCA was operated in the High Transmission Mode (HTM) [3] at a pressure of 0.4 mbar He. After passing a 14 cm x 4 cm large Mylar window of 1.2 μm thickness, evaporation residues were thermalized in He at 1200 mbar in a newly designed recoil transfer chamber (RTC) of 1.7 cm depth. The RTC had two funnel shaped inlets at the right and left hand side for the He/KCl jet and a central outlet in the cover plate. The Rf was transported to ARCA by a He/KCl jet through a 10 m long PE capillary of 2 mm i.d. at a gas flow rate of 2.9 L/min. To monitor the gas-jet yield, a ²²⁷Ac emanation source was connected to the RTC. Ar with a flow rate of 20 mL/min was passed through the source and transported ²¹⁹Rn into the RTC. The yield of its decay product ²¹¹Bi was compared to the respective yield in ROMA [4]. The ²¹¹Bi yield in ARCA including collection, dissolution in 7x10⁻⁴ M HF solution, and evaporation on a Ta disc was 50% of that in ROMA.

For the anion-exchange chromatography in ARCA, the column magazines were filled with the resin MCI GEL CA08Y from Mitsubishi Chemical Corporation, particle size 22±5 μm, which was transferred into the hydroxide form as described in [5]. In each chromatography experiment, two Rf fractions were collected. The first one was 7x10⁻⁴ M HF, which was also used for column loading, and the second one was 5 M HNO₃. The latter was used to strip the remainder of the Rf from the column. After around 18 h experiment, the concentration of the first solution was changed to 1x10⁻³ M HF and the experiments were continued for another 25 h.

The KCl clusters were collected in ARCA for 90 s. Within this time, the column for the next experiment was preconditioned for 65 s with the HF solution. After the collection, the products were dissolved in 200 μl of 7x10⁻⁴ M HF solution and were subsequently fed onto the anion-exchange column at a flow rate of 1.0 mL/min. The effluent of the column was collected on a Ta disk as fraction 1. The fraction of the products adsorbed on the resin was eluted with 250 μL of 5 M HNO₃ and collected on a

second Ta disk. Both fractions were evaporated to dryness by infrared light and a hot helium stream. The two Ta discs were then subjected to α-spectroscopy. Counting of the first fraction started 60 s after the end of the collection interval, counting of the second fraction started 65 s after the end of the collection.

In total, seven α-events were detected which we attribute to 78-s ^{261a}Rf based on the measured α-energy and lifetime. All of them were observed in the HNO₃ fraction. Two of these events were detected during the experiments with 7x10⁻⁴ M HF, the other five events were detected while using 1x10⁻³ M HF. As no events were observed in the HF fractions, it is only possible to give a lower limit for the %ads value. As in Poisson statistics zero observed events are compatible with three events at 95% confidence level, 3 events were assumed for the first fraction and the remainder in the second fraction resulting in %ads ≥ 62.5 % in 7x10⁻⁴ M HF and %ads ≥ 72.5 % in 1x10⁻³ M HF. The sum of the α events is shown in Figure 1 indicating that the α spectra were very clean, also thanks to preseparation in TASCA.

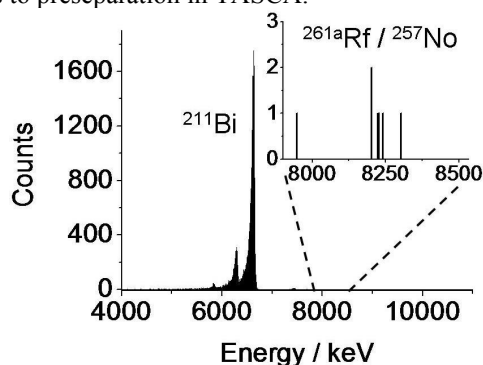


Figure 1: Sum spectrum of the α-particle events of ^{261a}Rf.

From a comparison with the number of ^{261a}Rf events in ROMA, we have to conclude that the chemical yield in ARCA was low, on the order of 30% only. This is in line with earlier observations indicating some sorption of transactinides from HF solutions on the Kel-F slider in ARCA.

References

- [1] M. Schädel *et al.*, contribution to this report.
- [2] M. Schädel *et al.*, *Radiochim. Acta* **48**, 171 (1989).
- [3] A. Semchenkov *et al.*, *NIM B* **266**, 4153 (2008).
- [4] A. Gorshkov *et al.*, this report.
- [5] A. Toyoshima *et al.*, *Radiochim. Acta* **96**, 125 (2008)

* Work supported by BMBF (06MZZ231) and GSI-F&E (MZJVKR)

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Die Herstellung von Plutoniumtargets für TASCA durch Elektrodeposition*

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Am TransActinide Separator and Chemistry Apparatus TASCA bei der GSI können durch Fusionsreaktionen mit Aktinidentargets Transaktinidenelemente ($Z > 103$) hergestellt werden. An TASCA wird dazu ein aus drei bananenförmigen Segmenten mit einer aktiven Fläche von je $1,74 \text{ cm}^2$ bestehendes, rotierendes Targetrad benutzt. Eine $2 \mu\text{m}$ dicke Ti-Folie dient als Backing für die Elektrodeposition des Targetmaterials.

Kürzlich ist gezeigt worden, dass an TASCA die Produktion von Rf in der Reaktion $^{244}\text{Pu}(^{22}\text{Ne}, 4-6n)^{260-262}\text{Rf}$ möglich ist [1]. In naher Zukunft soll das Element 114 durch die Reaktion $^{244}\text{Pu}(^{48}\text{Ca}, 4n)^{288}114$ produziert und seine chemischen Eigenschaften untersucht werden.

Da ^{244}Pu nur in sehr begrenzten Mengen erhältlich ist, muss die Targetherstellung mit hohen Ausbeuten erfolgen. Zur Optimierung der Parameter für die elektrochemische Abscheidung von Pu auf einer Ti-Oberfläche, werden die Experimente zunächst mit dem in größeren Mengen vorhandenen Isotop ^{239}Pu durchgeführt.

In einem Teflonbecher wird $1,5 \text{ ml}$ einer ^{239}Pu -Lösung ($1,25 \text{ mg Pu}$ in 8 M HCl) zur Trockene eingedunstet. Der Rückstand wird mit $100 \mu\text{l}$ warmer $0,5 \text{ M HNO}_3$ aufgenommen und mit $100 \mu\text{l}$ $0,1 \text{ M HNO}_3$ in die Platingzelle überführt. Mit $800 \mu\text{l}$ Isopropanol wird der Teflonbecher gespült und die Lösung ebenfalls in die Platingzelle überführt. Diese wird dann mit 15 ml Isobutanol auf insgesamt 16 ml aufgefüllt.

Die Platingzeit beträgt 6 Stunden . Dabei wird die Stromdichte auf $1,15 \text{ mA/cm}^2$ begrenzt (entsprechend einer Stromstärke von 2 mA). Versuche haben gezeigt, dass bei höheren Stromdichten die Pu-Schicht nicht fest auf der Ti-Unterlage haftet. Die Spannung beträgt am Anfang 160 V und am Ende der Platingzeit bis zu 370 V .

Während der Deposition werden in einem Abstand von einer Stunde $10 \mu\text{l}$ der Lösung entnommen und daraus ein α -Präparat hergestellt. Dadurch kann die Pu-Konzentration in der Lösung verfolgt werden.

Nach dem oben beschriebenen Schema kann man eine Ausbeute von 68% bis 90% erreichen. Die Massenbelegung der so hergestellten Targets wird mithilfe einer α -spektroskopischen Messung bestimmt und beträgt 350 bis $500 \mu\text{g/cm}^2$. Bei einer Massenbelegung von mehr als $600 \mu\text{g/cm}^2$, löst sich die entstandene Pu-Schicht nach dem Trocknen des Targets wieder von der Ti-Folie ab.

Die Homogenität der Schicht wird mittels Radiographie untersucht [2]. Dazu wird das Gerät FLA 7000 der FUJIFILM Corporation benutzt. Es konnte so gezeigt

werden, dass bei Targetdicken bis zu ca. $500 \mu\text{g/cm}^2$ das Targetmaterial sehr homogen auf dem Backing verteilt ist. Abb. 1 zeigt, dass die Abweichungen im Bezug auf die Massenbelegung $\leq 10\%$ betragen.

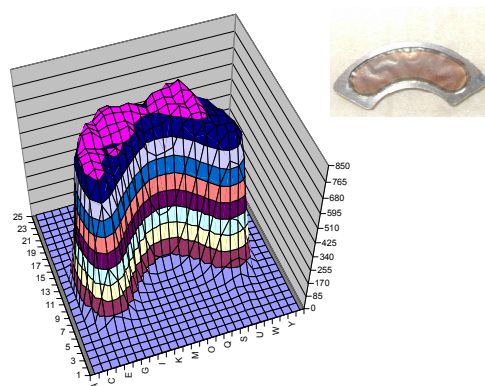


Abb. 1: Radiographie und Photographie eines Targets mit $500 \mu\text{g/cm}^2$

Das zur Abscheidung verwendete ^{244}Pu enthält u.a. auch geringe Mengen ^{241}Pu und damit auch ^{241}Am , welches durch seine hohe spez. Aktivität wesentlich zur Gesamtaktivität des Targets beiträgt. Zur Untersuchung des Abscheideverhaltens von Am neben Pu wurde vor der Abscheidung ^{241}Am -Tracer zur ^{239}Pu -Lösung zugegeben. Es konnte bestätigt werden, dass die Deposition von ^{241}Am und ^{239}Pu parallel stattfindet, siehe Abb. 2.

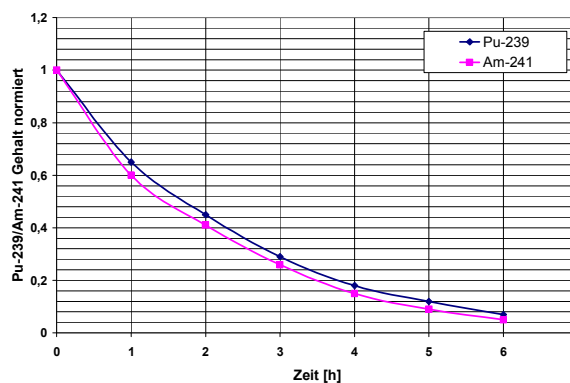


Abb. 2: Gleichzeitige Abscheidung von ^{239}Pu und ^{241}Am

Literatur

- [1] Even, J. et al, First Transactinide Chemistry Behind TASCA, Jahresbericht GSI, 2008
- [2] Liebe, D. et al, Improvements at the radiographic analysis of radioactive targets, Jahresbericht UMZ, 2006

*Gefördert im Rahmen eines Forschungs- und Entwicklungsauftrags der GSI (Projekt MZJVKR).

Measurements of $^{260-262}\text{Rf}$ produced in $^{22}\text{Ne} + ^{244}\text{Pu}$ fusion reaction at TASCA*

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As a final experiment in the commissioning phase of TASCA the transactinides ($Z \geq 104$) were reached. Production and decay of ^{260}Rf , $^{261a,b}\text{Rf}$ and ^{262}Rf [1,2,3], produced in the asymmetric nuclear fusion reaction $^{244}\text{Pu}(^{22}\text{Ne},\text{xn})$ was studied. Separated reaction products were guided to a Focal Plane Detector (FPD) or into a Recoil Transfer Chamber (RTC), where they were available for transport to either the Rotating wheel On-line Multidetector Analyzer (ROMA) or to the Automated Rapid Chemistry Apparatus (ARCA) for chemical experiments [4].

TASCA was operated in the High Transmission Mode (HTM) [5]. The ^{22}Ne ion beam (average intensity: $0.8 \mu\text{A}_{\text{part}}$) impinged on a rotating target wheel with 0.4 mg/cm^2 $^{244}\text{PuO}_2$ targets on $2.2 \mu\text{m}$ Ti backings. Three beam energies in the center of the target, $E_{\text{c.o.t.}}$, of 109 MeV, 116 MeV and 125 MeV, were used for the production of ^{262}Rf , ^{261}Rf and ^{260}Rf , respectively. The transmission of Rf has been optimized in He filling gas. The optimal pressure was 0.4 mbar. The magnetic rigidity, $B\rho$, was determined to be 1.99 T·m. To increase suppression of unwanted products, a He/H₂ (2:1) filling gas at a pressure of 1.5 mbar was used in experiments with the FPDs. Evaporation residues were implanted into a (80 x 36) mm² 16-strip Position-Sensitive silicon Detector (PSD) or a (58 x 58) mm² Double-Sided Silicon Strip Detector (DSSSD). In other experiments, $^{261a,b}\text{Rf}$ passed a 1.2 μm thick (140 x 40) mm² Mylar window and was thermalized in 1.2 bar He in the RTC (depth: 17 mm). Rf atoms were then transported to ROMA by an He/KCl jet (gas flow rate: 3.45 L/min) through a 4 m long polyethylene capillary (inner diameter: 2 mm).

The measurement of ^{260}Rf , produced in the 6n evaporation channel at $E_{\text{c.o.t.}} = 125$ MeV yielded 15 time ($\Delta t \leq 200$ ms) correlated EVR-SF events in the PSD. The correlation time analysis yielded a half-life of $21_{-4.3}^{+7.3}$ ms (errors are within the 68% confidence interval). A search for ^{262}Rf decays at $E_{\text{c.o.t.}} = 109$ MeV 7 position and time correlated EVR-SF events observed in the DSSSD, with EVR energies of 0.8 to 3.3 MeV and SF fragment energies of > 100 MeV. The measured $T_{1/2}$ for ^{262}Rf is 210_{-58}^{+128} ms (Fig. 1a), in contradiction with values from [1,2]. In addition, 9 short EVR-SF correlations were registered with $\Delta t \leq 1.5$ ms and EVR energies of 7.5 ± 5.0 MeV. They were attributed to the decay of $^{244\text{mf}}\text{Am}$ ($T_{1/2} =$

0.9 ms). Because of a relatively high counting rate of EVR-like events in the DSSSD a random event analysis was performed for EVR-SF correlations within a Δt of 1 s. The random event number, n_b , was calculated individually for each observed event. It varies between 0.035 and 0.11 and depends on the event position in the DSSSD.

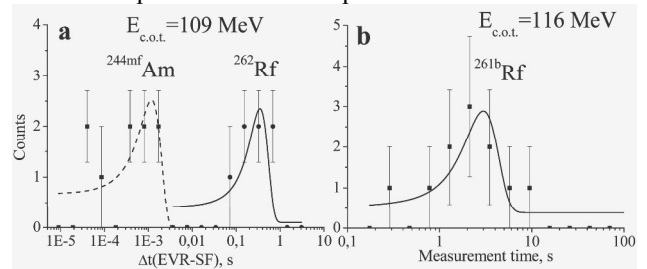


Figure 1: Time distributions of a) EVR-SF correlations from the DSSSD and b) SF decays from ROMA.

^{261}Rf was produced in the 5n channel at $E_{\text{c.o.t.}} = 116$ MeV and was detected in ROMA. Stepping time of 35 s (for ^{261a}Rf) were used. 149 single α -particles ($E_\alpha = 7.8 - 8.5$ MeV) from ^{261a}Rf and ^{257}No were registered; among these 28 α - α correlations. Also, 11 SF-events were registered and are attributed to ^{261b}Rf based on the measured $T_{1/2}$ of $2.2_{-0.5}^{+0.9}$ s. The SF activity assigned in [2] to ^{262}Rf likely originated from then unknown ^{261b}Rf .

From our results and cross section of 4.4 nb [6], a transmission of Rf through TASCA to a 140 x 40 mm² large area in the focal plane of 10% follows. For ^{261b}Rf , a cross section of $1.8_{-0.4}^{+0.8}$ nb was calculated, respecting decay during transport. With an estimated transmission of 6% to the area of the FPDs, preliminary cross sections for ^{260}Rf and ^{262}Rf of ≈ 1.2 nb and ≈ 250 pb, respectively, follows ^{261b}Rf was observed for the first time as an EVR. The production ratio of ^{261a}Rf to ^{261b}Rf is about 2.5:1. The data analysis is still in progress.

References

- [1] L. P. Somerville *et al.*, Phys. Rev. C **31**, 1801 (1985).
- [2] M. R. Lane *et al.*, Phys. Rev. C **53**, 2893 (1996).
- [3] Ch. E. Düllmann, A. Türler., Phys. Rev. C **77**, 064320 (2008).
- [4] J. Even *et al.*, this Scientific Report.
- [5] A. Semchenkov *et al.*, NIMB **266**, 4153 (2008).
- [6] Yu. Lazarev *et al.*, Phys. Rev. C **62**, 064307 (2000).

* Work supported by BMBF project 06MT248.

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A new TASCA focal plane detector*

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The new, highly efficient, gas-filled TransActinide Separator and Chemistry Apparatus (TASCA) has been recently put into operation at GSI with the aim to study chemical and physical properties of superheavy elements with $Z \geq 104$. Based on the results of magnetic field model calculations of the dipole and the quadrupoles, two modes of operation of TASCA, the "High Transmission Mode" and the "Small Image Mode" have been realized [1]. Two types of focal plane detector setups (FPD) were used during the TASCA commissioning phase: a $(80 \times 36) \text{ mm}^2$ 16-strip position-sensitive silicon detector (PSD) and a $(58 \times 58) \text{ mm}^2$ double-sided silicon strip detector (DSSSD) as a prototype for a new TASCA focal plane detector. The test experiments showed that the image size in the HTM is larger than the detector size of both detector types, as it was expected according to ion transport calculations and Monte-Carlo simulations [1,2]. The nominal vertical position resolution of the PSD is ± 0.2 mm. However, a search for position correlated decay chain members usually occurs within ± 1 mm limits, corresponding to a pixel size area of $(5 \times 2) \text{ mm}^2$. The relatively large pixel size of the PSD negatively affects search limits for rare decay chains from long-lived isotopes of superheavy elements. The TASCA FPD working group has decided to build a detector setup based on a DSSSD as a stop detector and a backward array consisting of single-sided silicon strip detectors (SSSD). A *veto* detector for light fast ions that penetrate the DSSSD will be mounted behind the stop detector. The new setup will feature a $(144 \times 489) \text{ mm}^2$ large detector, which will accept $> 90\%$ of all evaporation residues reaching the focal plane. The geometrical detection efficiency for α -particles emitted from implanted nuclei will be $> 70\%$. As compromise between a pixel size as small as possible and the number of spectrometric electronic channels as small as possible, a pitch width of 1 mm on the front and back side of the DSSSD has been chosen. To reduce the necessary number of ADCs the number of strips on each side of the DSSSD and on the SSSD should be a multiple of 8 when using 32-channel preamplifiers and 8 or 16-channel am-

plifiers with integrated multiplexers. A DSSSD structure with an active area of $(72 \times 48) \text{ mm}^2$ has 72 strips on the front side and 48 strips on the back side. The strip width and the interstrip distance on the both sides of the DSSSD are $900 \mu\text{m}$ and $100 \mu\text{m}$, respectively. Two adjacent DSSSDs form the stop detector with an active area of $(144 \times 48) \text{ mm}^2$. A SSSD structure with an area of $(72 \times 48) \text{ mm}^2$ has 8 strips, which are 72 mm long. The strip width and the interstrip distance of the DSSSD are 5.65 mm and $100 \mu\text{m}$, respectively. 8 SSSD detectors form the backward array with a depth of 72 mm. Two similar SSSD detectors are used as *veto* detector. Silicon wafer thicknesses of $300 \mu\text{m}$ and $500 \mu\text{m}$ have been chosen for the DSSSDs and SSSDs, respectively. These thicknesses will allow for the detection of conversion electrons in the backward array. A schematic design of the new TASCA detector array and first results from source measurements are shown in Fig. 1.

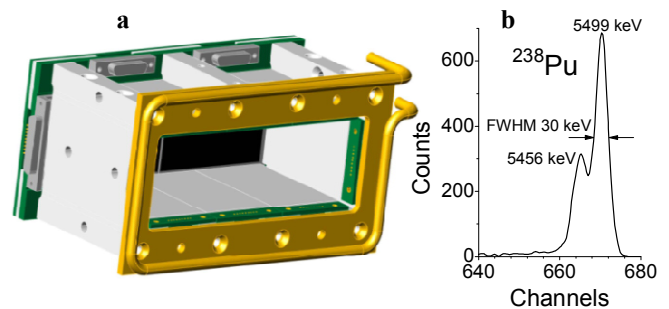


Figure 1: A drawing of the new TASCA FPD array (a) and an alpha particle spectrum from a DSSSD strip (b).

In total, the new TASCA detector array has to process the signals of 320 strips. The necessary spectrometric and data readout electronics, which are compatible with TAsISpec [3], as well as the associated software, should be ready for experiments in spring 2009.

References

- [1] A. Semchenkov et al. NIM B **266**, 4153 (2008).
- [2] K. Gregorich et al. GSI Sci. Rep. 2006, 144 (2007).
- [3] L.-L. Andersson et al., this report.

* Work supported by BMBF project 06MT248.

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TASISpec - A new twist on spectroscopy of superheavy elements.

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A new nuclear spectroscopy set-up called TASISpec (*TASCA Small Image mode Spectroscopy*) has been designed and commissioned. It exploits TASCA's specific small image focal mode, i.e. the fact that superheavy elements (SHE) produced in fusion-evaporation reactions can be focused into an area of less than 3 cm in diameter. This provides the world-unique possibility to pack composite Ge-detectors in very close geometry, resulting in an unprecedented, highly efficient detection of γ -rays and X -rays in coincidence with implanted SHE.

The test set-up as used in 2008 is illustrated in Fig. 1. It comprised four single sided silicon strip detectors (SSSD), one double sided silicon strip detector (DSSSD) and two Ge detectors; one cluster (7 crystals) downstream and a large VEGA clover (4 crystals) on one side. The final set-up foresees additional three clover detectors, while their implementation requires a dedicated holding structure to be built in 2009.

Conversion electron, γ -ray, and α sources as well as parasitic beams inducing the reactions $^{206}\text{Pb}(^{48}\text{Ca}, 2n)^{252}\text{No}$, $^{207}\text{Pb}(^{48}\text{Ca}, 2n)^{253}\text{No}$, $^{244}\text{Pu}(^{48}\text{Ca}, 4n)^{288}114$, and $^{150}\text{Nd}(^{64}\text{Ni}, xn)^{214-x}\text{Ra}$, $^{154}\text{Sm}(^{64}\text{Ni}, yn)^{218-y}\text{Th}$, $^{nat}\text{Gd}(^{64}\text{Ni}, zn)^{224-z}\text{U}$, have been used to start to characterise the performance of TASISpec. Detection efficiencies amount to some measured 80% for emitted α particles and extrapolated more than 40% (absolute scale) for γ rays at an energy around 250 keV. In addition, energy thresholds of particle- and γ -ray detectors, dead times, and data rates of a first combined VME (up to 224 channels for Si-strip detector processing) and XIA-DGF (11 channels sampling the Ge-detector signals) data acquisition system were successfully tested as well as TASCA-SIM transmissions determined at different magnet settings.

In 2009 it is planned to establish the extraordinary $\gamma\gamma$ -, γ -EC-, EC-EC, or even $\gamma\gamma$ -EC-, multi-coincidence capabilities of the both segmented and compact TASISpec set-up by settling the decay scheme of K -isomeric states in ^{253}No [1, 2, 3, 4]. Despite of the underlying amount of data many question marks still remain regarding the structure of ^{253}No .

Following upon this ideal starting point to show the proof-of-principle of TASISpec, K isomers expected in neutron-rich SHE around ^{270}Hs [5] will be stepwise approached via, e.g., spectroscopic studies of $^{255,257}\text{No}$, ^{261}Rf , and ^{265}Sg . Such a programme employs also the

unique facets of both high UNILAC beam intensities, use of radioactive actinide targets, and high transmission of TASCA for rather asymmetric reactions. Last but not least, the unprecedented γ -efficiency of TASISpec may allow to discriminate SHE by means of characteristic X -rays.

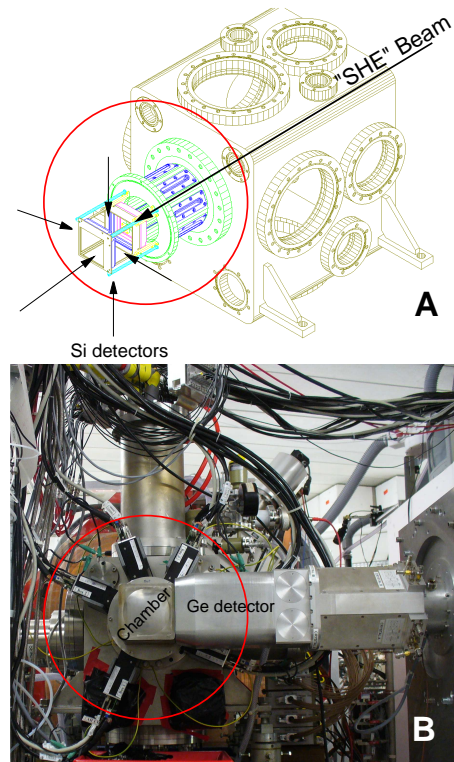


Figure 1: The TASISpec set-up installed at the focal plane of TASCA. Panel (A) illustrates a drawing of the end of the TASCA separator. The TASISpec structure is encircled. Five silicon strip detectors are placed in a cube-like shape. Panel (B) shows a photograph of the commissioning set-up. To the right a Ge-VEGA-clover detector is placed.

References

- [1] F. P. Hessberger *et al.*, *Eur. Phys. J. A* **22**, 417 (2007).
- [2] R.-D. Herzberg *et al.*, *Eur. Phys. J. A* **15**, 205 (2002).
- [3] F. P. Hessberger, *Physics of Atomic Nuclei* **70**, 1445 (2007).
- [4] A. Lopez-Martens *et al.*, *Eur. Phys. J. A* **32**, 245 (2007).
- [5] J. Dvorak *et al.*, *Phys. Rev. Lett* **97**, 242501 (2006).

Observation of ^{270}Hs in the complete fusion reaction $^{36}\text{S}+^{238}\text{U}^*$

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Superheavy elements ($Z \geq 104$) exist only due to nuclear shell effects. Deformed shell closures at $Z=108$ and at $N=162$ have been predicted theoretically [1] and observed in recent experiments [2]. Three hassium isotopes, $^{269-271}\text{Hs}$, have been produced in the complete fusion reaction $^{248}\text{Cm}(^{26}\text{Mg}, \text{xn})^{274-x}\text{Hs}$ at the linear accelerator UNILAC at GSI [2,3]. The excitation function measurement at five different beam energies resulted in maximum cross sections of the 3n, 4n, 5n exit channels of a few pb.

Recent theoretical studies, analysing the formation of ^{270}Hs in the 4n channel, using a two-parameter Smoluchowski equation, predict even higher cross sections for the reaction $^{238}\text{U}(^{36}\text{S}, 4n)^{270}\text{Hs}$ and $^{226}\text{Ra}(^{48}\text{Ca}, 4n)^{270}\text{Hs}$ in the order of a few tens of pb [4]. Due to a lower reaction Q-value, these calculations predict a maximum cross section of about 24 pb for the $^{238}\text{U}(^{36}\text{S}, 4n)^{270}\text{Hs}$ reaction, while the HIVAP code [5] predicts a maximum cross section of 3.5 pb.

Here, we report on first results of an experiment aimed to study the nuclear fusion reaction $^{36}\text{S} + ^{238}\text{U}$, leading to the compound nucleus $^{274}\text{Hs}^*$. For the experiment we used our highly efficient chemical separation and detection system COMPACT which was connected to a Recoil Chamber (RC) installed behind the ARTESIA target wheel in cave X1 [2]. A beam of $^{36}\text{S}^{5+}$ ions was accelerated by the UNILAC up to 7.13 MeV/u and impinged on a rotating ^{238}U target wheel. During the experiment, we used two different sets of ^{238}U targets. The beam passed through a 20.2 μm Be vacuum window, 6 mm of He/O₂ gas mixture (He:O₂ = 9/1), a 12.6 μm Be target backing before entering the ^{238}U target (3 segments of 1.8 mg/cm², 1.5 mg/cm² and 1.6 mg/cm²). The second target set had a Be backing of 8.2 μm and 3 segments containing 1.0 mg/cm² of ^{238}U each. We assumed that only Hs nuclei with a minimum residual range after exiting the target of 10 mm in gas could be transported to the detection system, corresponding to an active layer of the target of 1.0 mg/cm². The energy of the ^{36}S ions was in the range of 175.0 MeV to 181.2 MeV within the first set of target and in the range of 190.4 MeV to 196.1 MeV in the second set [6], corresponding to excitation energies, E^* , of 38 ± 3 MeV and 51 ± 3 MeV [7], near the predicted maxima of the 4n and 5n evaporation channel, respectively. Starting at $E^* = 38$ MeV we irradiated the first target set with a beam dose of $5.74 \cdot 10^{17}$ ions. The second target set was irradiated with a beam dose of $1.03 \cdot 10^{18}$ ions at $E^* = 51$ MeV.

The data analysis revealed one correlated chain at the higher E^* of 51 MeV. A 9.02 ± 0.05 MeV α -particle was observed in bottom detector #24 followed after 23 ms by one 41 MeV spontaneous fission fragment measured in the top detector #24. Due to the measured properties we attributed this decay chain to the decay of ^{270}Hs produced in the 4n evaporation channel [2].

Because of background from α -decay and SF of heavy nuclides ($A > 200$) from (multi) nucleon transfer pseudo correlated chains can be found with nonzero probability. We have searched for possible random decay chains $\alpha \cdot \alpha \cdot \alpha \cdot \alpha$, $\alpha \cdot \alpha \cdot \text{SF}$ and $\alpha \cdot \text{SF}$, using subsequent time windows of 300 s length each. α -particles in an energy window $8.0 \leq E_\alpha \leq 9.5$ MeV and SF-like events with at least one fragment above a threshold of 15 MeV were considered. 351 and 771 α -particles have been registered in the first and the second run, respectively. Mainly this background was attributed to α -decays of ^{212}Po . In addition, 6 SF-like events were registered in the first run and 13 events in the second run. None of these high energy events were correlated in time and position to each other. The results are shown in Table 1.

Table 1: Random rates for different decay chains

decay chain	$E^* = 38$ MeV	$E^* = 51$ MeV
$\alpha \cdot \alpha \cdot \alpha \cdot \alpha$	$7.08 \cdot 10^{-4}$	$3.12 \cdot 10^{-3}$
$\alpha \cdot \alpha \cdot \text{SF}$	$4.61 \cdot 10^{-3}$	$1.67 \cdot 10^{-3}$
$\alpha \cdot \text{SF}$	$1.6 \cdot 10^{-2}$	$4.6 \cdot 10^{-2}$

At $E^* = 38$ MeV the cross section limit for both channels is 2.9 pb. The cross section for the 4n channel at $E^* = 51$ MeV based on the one event is $0.8_{-0.7}^{+2.6}$ pb and the cross section limit for the 5n channel is 1.5 pb. Errors and limits correspond to 68% confidence level. The measured cross section and cross section limits are lower than for the reaction $^{248}\text{Cm}(^{26}\text{Mg}, \text{xn})^{274-x}\text{Hs}$ [3], especially for 5n evaporation channel, in contrast to calculations made in [4]. We plan to continue these measurements in the near future.

References

- [1] Z. Patyk, A. Sobiczewski, Nucl. Phys. A 533, 132 (1991).
- [2] J. Dvorak *et al.*, Phys. Rev. Lett. 97, 242501 (2006).
- [3] J. Dvorak *et al.*, Phys. Rev. Lett. 100, 132503 (2008).
- [4] Z. H. Liu, J.-D. Bao, Phys. Rev. C 74, 057602 (2006).
- [5] W. Reisdorf, M. Schädel, Z. Phys. A 343, 47 (1992).
- [6] J.F. Ziegler, Nucl. Instr. and Meth. A 219, 1027 (2004).
- [7] G. Audi *et al.*, Nucl. Phys. A 729, 337 (2003)

* Work supported by BMBF project 06MP2471

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Liquid – liquid – extraction with the MicroSISAK – system

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In previous experiments it could be demonstrated that continuous liquid – liquid – extractions on a μl scale are possible with the MicroSISAK device [1]. Recently the IMM developed an improved version of this so called microreactor with two different mixer designs and up to three consecutive separation stages. A scheme of the setup for the experiments is shown in figure 1.

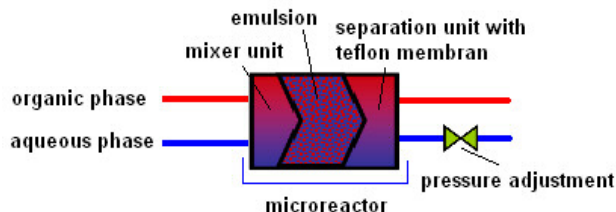


Figure 1: Scheme of the MicroSISAK setup

A static interdigital mixer is used for the formation of small droplets [2]. The formed emulsion is then separated by using a hydrophilic teflon membrane. A backpressure at the outlet of the aqueous phase corresponds to the internal pressure in the MicroSISAK device. This has an effect on the separation at the membrane. The inner volume of the used so far needle valve is much larger than the volume of the mixer, thus it is not possible to adjust a definite and reproducible backpressure in the separation unit.

Therefore a new apparatus was designed to set backpressure on the aqueous outlet of the microreactor by a gas volume. A standard vial made of polyethylene-terephthalate is equipped with three holes in the upper sealing cap: one as inlet for the aqueous phase coming from the reactor, and two for gas in and out. One hole in the bottom serves as liquid outlet (Fig. 2).

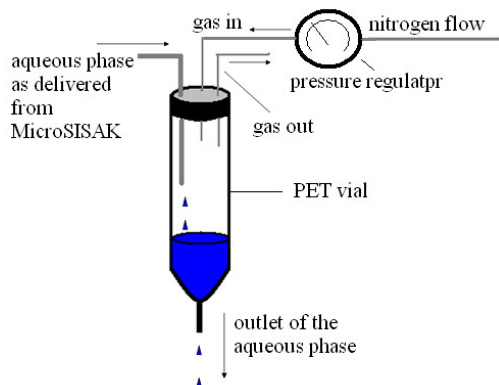


Figure 2: Scheme of the new pressure regulation apparatus.

The pressure in the vial is controlled with a high precision pressure regulator. It is reproducible with an accuracy of 5 mbar.

For studies on the extraction yield for hafnium – the lighter homologue of rutherfordium (Rf) $Z = 104$ – we have chosen an extraction system, that has successfully been applied in chemical investigations of Rf with SISAK [3]: Extraction of hafnium (Hf) with trioctylamine (TOA)

in toluene from dilute sulphuric acid. While keeping the TOA concentration constant, the concentration of the acid was varied from 0.05 mol/l to 2 mol/ml. In order to measure the extraction yield Hf-181 is used as a tracer. Its activity in the organic phase is compared to the total activity in both phases. From this one can calculate the extraction efficiency. The main results of the batch experiments are shown in the upper line of figure 3. The results of the extraction experiments with the microreactor (lower part of figure 3) compare to the one in the batch experiments relating to the concentration of the two solutions.

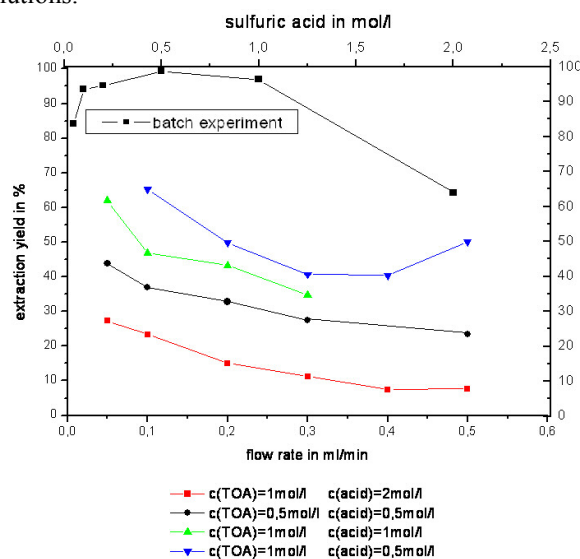


Figure 3: Extraction of Hf-181 with TOA: The upper line shows the extraction yield by varying the concentration of the sulphuric acid and a constant concentration of TOA (1 mol/l). The lower part: the extraction yield depends on the flow rate for different concentrations of the TOA and sulphuric acid.

One can observe a decrease of the extraction yield with increasing flow rates. At flow rates below 1 ml/min phase mixing is inefficient, thus extraction yield is low and mainly depends on the hold-up time in the mixer. At flow rates higher than 1 ml/min, smaller droplets are formed in the mixer. Thereby an emulsion is created and a much higher extraction yield can be expected. Corresponding experiments are currently carried out.

Acknowledgement:

I would like to thank the mechanical workshop of our institute for the realisation of the new pressure regulation apparatus.

References:

- [1] K. Eberhardt et al., Institut für Kernchemie der Universität Mainz, Annual Report A8 (2005)
- [2] W. Ehrfeld, V. Hessel, H. Löwe, Microreactors, Wiley-VCH, 2000
- [3] L. Zheng et al., Radiochimica Acta 96, 41-48 (2008)

Prototype developments for a high-resolution neutron detector at R³B

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INTRODUCTION

A detector for momentum measurements of high-energy neutrons in the energy range 200 MeV to 1000 MeV is being developed for the R³B experiment at FAIR. The detection principle is based on a combination of converter material and subsequent detection of charged particles from reactions in the converter material. Multi-gap Resistive-Plate Chambers (MRPC) are used for the detection of charged particles. A modular system with about 10'000 electronic channels is considered. The total depth of 1 m, 50% of which are high-Z converter (nuclear interaction length ~ 17 cm) ensures a detection efficiency close to 100% for neutron energies above 200 MeV. The detector is subdivided into 60 planes with active areas of 2×2 m² adding up to a total area of 240 m² MRPC modules. A time resolution of the full detector below $\sigma = 100$ ps and a spatial resolution of less than 1 cm in all three dimensions are desired. In addition, the detector should provide a good efficiency for detecting and reconstructing multi-neutron events.

NeuLAND pre-design based on MRPC

The detection concept for the new neutron detector relies on the combination of converter plus detection material, as also realized in the current detector for fast neutrons LAND (Blaich et al.). A detector composed out of active material only has been considered in the preparatory phase of the R³B Technical Proposal. In principle a dense scintillation material like PbWO₄ would be well suited for combining converter and scintillator in one homogeneous layer. However, the high costs as well as the timing properties of the scintillator rule out this option.

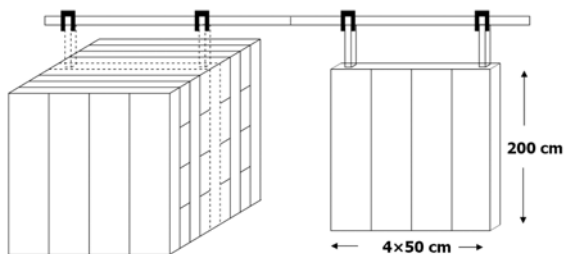


Figure 1: Schematic drawing of the modular structure of the NeuLAND detector.

Resistive Plate Chambers (RPC) are detectors for ionizing particles and presently these types of detectors are used in many different experiments involving cosmic rays and accelerators such as STAR, RICK, CMS and ATLAS at LHC, CERN, AGRO etc. Excellent time resolutions down to $\sigma_t < 50$ ps were achieved for minimum ionizing particles using multi-gap resistive plate chambers (MRPC). Large detector arrays with high granularity are feasible, thus the MRPC detector systems partly take over the classical application of scintillators for ToF-arrays. A. Blanco et al. showed that a large area MRPC (160 cm \times 10 cm, 2 strip readout) can provide good time resolutions of $\sigma_t \sim 50$ -70 ps and a position resolution of 1.2 cm along the strips using the time difference method. In addition, an efficiency for minimum ionizing particles of more than 95% was achieved.

The present design concept foresees a modular structure of MRPC modules with a size of 200×50 cm² each. Four modules build up one detector plane (s. Figure 1).

Prototype development and tests at FZD

The Forschungszentrum Dresden-Rossendorf (FZD) is involved in building and testing MRPC structures capable of sustaining high rates (R. Kotte et al.), as they are expected in the CBM experiment. Now the development of MRPC prototypes with intrinsic neutron converter structure for the NeuLAND detector at FAIR is under investigation. The 40 MeV electron beam from the ELBE facility at FZD with its picosecond time structure is used as a high-intensity defined source of minimum ionizing particles. The timing of the prototypes built at FZD and also at GSI is studied in regular short beamtimes at ELBE.

Based on the R³B-Technical Proposal a first prototype has been developed where design decisions can be verified experimentally. As converter material for producing charged particles from the initial high-energy neutrons, stainless steel has been selected due to its good handling and commercial availability in pre-cut sizes. For the actual MRPC structure, commercial float glass (0.55 mm thick) has been used, with 0.3 mm diameter standard fishing line as spacer. All prototypes tested so far had an active area of 200×400 mm. Figure 2 shows the result of a measurement of the time resolution.

* Work supported by BMBF (06MZ222I), (06DR134I), (06DA129I)
GSI FuE DR-GROS

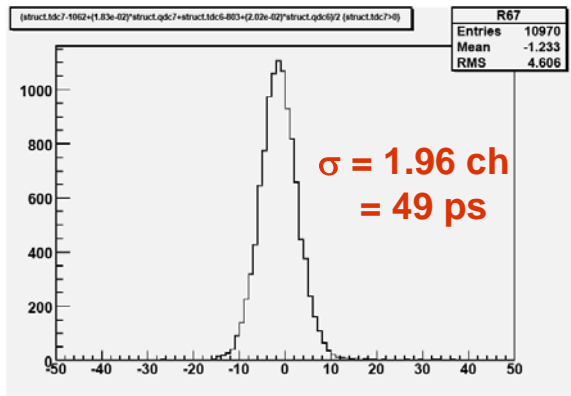


Figure 2: Typical time spectrum of a NeuLAND prototype with single-ended readout after applying a linear walk correction.

Prototype developments and tests at GSI

The prototype constructed at GSI is similar to the FZD type, but addresses some different aspects concerning in particular number of gaps, distances between anodes strips, and impedance matching.

The active area is $400 \times 200 \text{ mm}^2$, subdivided in 8 anode strips, each 400 mm long, 25 mm wide and 4 mm thick Fe-material, acting as the same time as converter for the neutrons. The distance between the anode wires is kept to a minimum value of 0.3 mm, which is essential in terms of converter and detection efficiency. We use 2×4 gaps, built from 0.55 mm glass plates and gap sizes of 0.3 mm using fishing lines as distance holders (Figure 3).

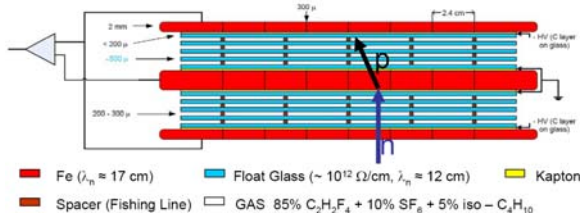


Figure 3: Schematic view of the GSI prototype.

The outer electrodes are 2mm thick Fe-plates, again acting as a converter at the same time. The high voltage is applied through a semiconductive layer which is sprayed on the outer glass plates.

One critical issue addressed is the impedance matching of the anode wires to the frontend electronics. The impedance of the anode wires was determined with a signal analyser to be 9.5Ω . This value has to be compared with the typical input impedance of the electronics is 50Ω . Measurements of the behaviour of the signal reflection and transmission as a function of the frequency of the signal in case of no impedance matching between anode strips and readout were performed using a network analyser. The transmission was found to be below 10% for most of the frequencies and high frequencies play a dominant role for the excellent timing properties.

In order to improve the signal transmission, the use of transformers or resistor networks for the purpose of adapting the impedances were investigated. For the high bandwidth transformer TC 4-11 a decrease of reflections to values below 10% was found for a wide range of frequencies. Because of this promising result the transformers were coupled to the anode strips using a special type of PCB board. The measurements with the network analyser show that reflection and transmission of the combination of anode strip and transformer board are significantly improved, but not for the full bandwidth (Figure 4).

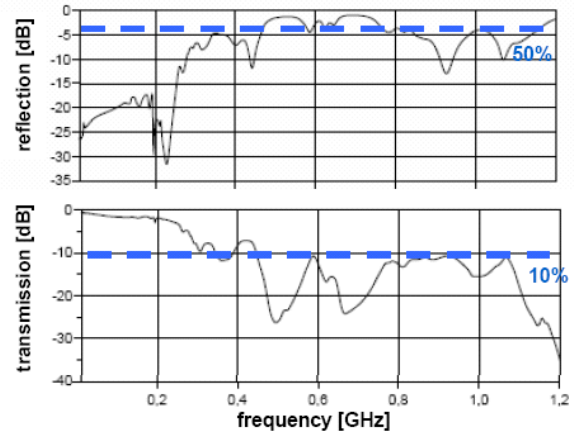


Figure 4: Presented here are the reflection and transmission properties as a function of frequency for the anode strip read out via the transformer board.

Gas recycling concept

The standard gas mixture for timing MRPCs consists of 85% Reclin-134a (1,1,1,2-tetrafluoroethane), 10% SF_6 , and 5% isobutane ($\text{i-C}_4\text{H}_{10}$). Reclin with its high primary ionization density fulfills the role of the main ionization medium, whereas SF_6 serves as an electron scavenger for low energy electrons and isobutane is used as an UV photon quencher. Although Reclin and SF_6 both are neither flammable nor reactive or toxic, special attention has to be paid when using these gases since they contain a significant global warming potential (factor 103 and 105 versus CO_2 for Reclin, SF_6 respectively). Therefore technical solutions need to be found avoiding the emission of these two gases.

A pre-concept was developed to overcome this difficulty. Two variants of a gas recycling circuit are currently being discussed; both aim for a reuse of the gas mixture for the detector after cleaning and controlling the quality (s. contribution by D. Rossi et al.).

References

- A. Blanco et al., IEEE Trans. Nucl. Sci **48** (2001) 1249
- T. Blaich et al., NIM **A314** (1992) 136
- R. Kotte et al. NIM **A 564** (2006) 155

Prototyping of DSSD detectors for the EXL/R B collaboration

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Motivation

The EXL experiment as a part of future FAIR facility [1] will provide the means for studying many physics phenomena in unstable exotic nuclei. Reactions will be done in inverse kinematics using new storage-ring techniques and a universal detector system providing high resolution and large solid angle coverage for kinematically complete measurements. Our work focuses on prototyping and testing DSSDs as a part of EXL's Silicon Particle Array (ESPA) [2]. DSSD chips were manufactured at PTI St. Petersburg. In the course of technical development potential synergies in particular with the R³B experiment is expected.

Technical Procedure And Results

Within a first stage of prototyping eight detectors were built and tested. Four of these are of 64×64 strips type and the other four of 64×16 type, respectively with the first number referring to the P⁺ side and the second to the N⁺ side of the detector. Detector chips of active area of 21×21mm² are 300μm thick and have a strip pitch of 300μm for the 64 strips side and 1250μm for the 16 strips side, respectively. The same epoxy PCB was designed for

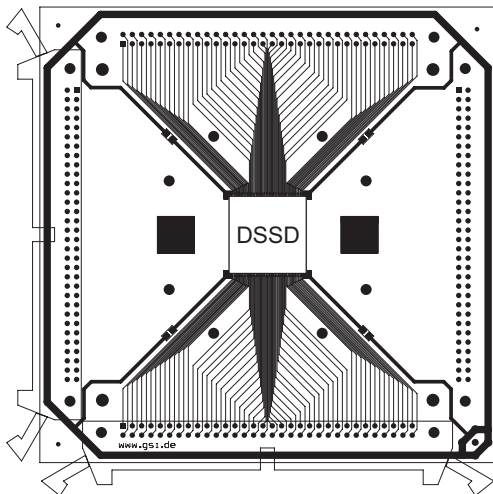


Figure 1: PCB layout for 64x64 and 64x16 DSSDs.

both types of DSSDs (see Fig. 1) with standard 64-way IDC connectors enabling to read signals from both sides. The chips were glued with a special low outgassing epoxy to a small step machined on the edge of the inner opening of the PCB and manually bonded. Biasing of the detector was done with the punch-through method using a bias ring surrounding the strips. Total depletion voltage was established

at -50V, but overbias of up to -200V was applied to the P⁺ side with AC-coupled preamps. The grounding through DC-coupled preamps was used on the N⁺ side. The read-out used 16 data channels on each side with 4 strips coupled together in the case of the 64 strip sides. Measurements in vacuum of about 3×10^{-7} torr were performed using a ²⁴¹Am α source.

Out of 752 tested strips 97 showed good spectroscopic properties. Using P⁺ (and N⁺) injection we achieved an energy resolution down to 15.6 keV (and 35.3 keV) for the P⁺ and 17.9 keV (and 44.6 keV) for the N⁺ side. Worse resolution for N⁺ injection is due to distorted field in between the N⁺ strips caused by P⁺ implants used to enhance interstrip isolation. Important part of our tests was the study of interstrip events on both sides of the detector whose induced signal is shared between two neighboring strips. Two dimensional correlation analysis of simultaneously occurring signals on both sides of the detector, i.e. P⁺ vs. N⁺ strips, was performed to evaluate the interstrip contribution. All events fall into four categories of: 1) strip-strip type with energy signal induced in a single strip on both sides of the detector, 2) strip-interstrip and 3) interstrip-strip type with N⁺ or P⁺ respectively, sharing the energy between two neighboring strips and 4) interstrip-interstrip type with both sides having the induced signal shared between two strips. The results show that for P⁺ injection strip-strip events and those events from strip-interstrip category induced on the P⁺ side of the detector contribute to about 95% of all events and have average resolution of 18.6 keV. The reconstructed energy $E_{strip1} + E_{strip2}$ from interstrip events has an average resolution of 195 keV and 82 keV and relative contribution of 5% and 20% for P⁺ and N⁺ side, respectively. Reconstructed interstrip-interstrip events have a resolution of 336 keV and represent 1% of all events. The percentage distribution of events corresponds within the error bars with the geometry of active and interstrip areas of our detectors. Our prototyping reveals good properties of tested DSSD chips and their usability in future EXL experiment. Further detailed tests as well as a proton beam experiment at KVI, Groningen using a telescope arrangement to test the tracking and energy reconstruction properties of our DSSDs together with Si(Li) detectors are scheduled for the first half of 2009.

References

- [1] **FAIR homepage:** http://www.gsi.de/fair/index_e.html
- [2] **EXL homepage:** <http://ns.ph.liv.ac.uk/mc/EXL/ns-instrument.html>

A closed-circuit gas system for an RPC-based neutron detector

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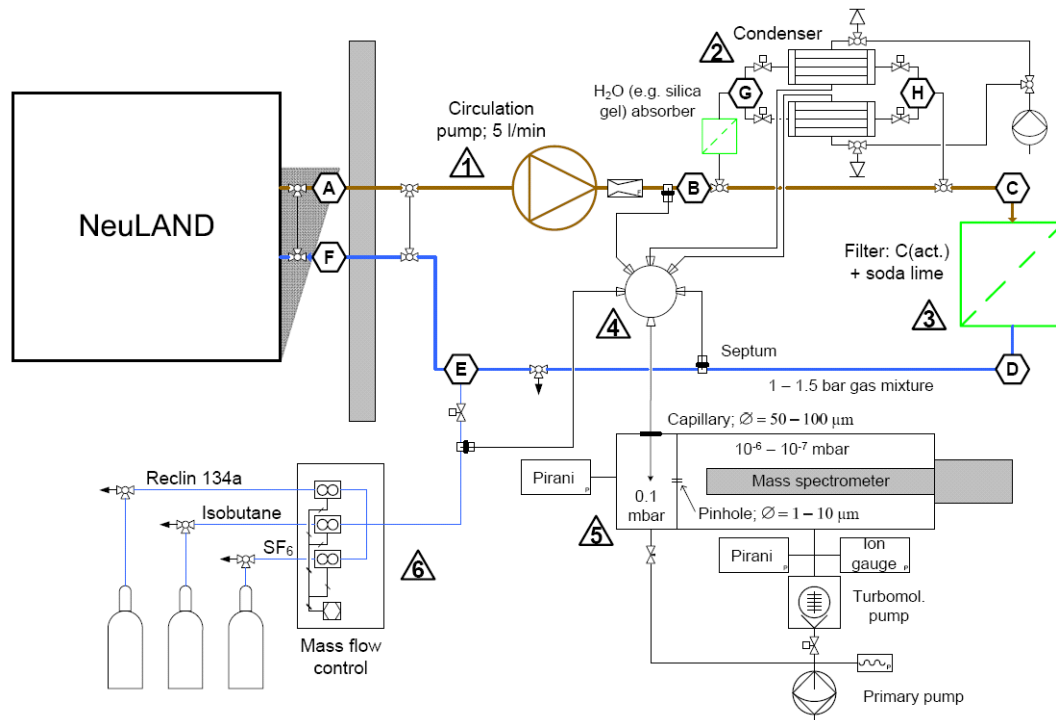


Figure 1: Proposed closed-circuit gas system for the NeuLAND neutron detector. For description, see text.

As a core component of the R³B experimental setup [1] in the future FAIR facility, a new neutron detector – NeuLAND – is currently under development at GSI. It is foreseen that NeuLAND will be based on a resistive plate chamber (RPC) concept. RPCs are gas detectors running on a gas mixture of approximately 85% Reclin 134a (1,1,1,2-tetrafluoroethane), 10% SF₆ and 5% Isobutane. Reclin 134a and SF₆ are both greenhouse gases, whose emission will be subject to emerging legal constraints. Even though a detector system such as NeuLAND is a negligible emitter of such gases, a closed-circuit gas system also improves the long-term stability of the gas mixture inside the detector, and reduces the total running cost of the detector, since only a limited amount of fresh gas needs to be supplied to the system.

The proposed closed-circuit gas system, as shown in fig. 1, would be located outside the experimental area, allowing maintenance even during an ongoing experiment. It consists of a main recirculation circuit (1), a condensation and storage sub-circuit (2), an analysis system (5) and an injection sub-circuit (6). Under normal operation (path: ABCDEF), the gas flow is driven by a circulation pump through a chemical filter (3) filled with activated charcoal and soda lime, removing gas contaminants produced by the RPCs.

One of the central issues in this closed-circuit gas system is the continuous monitoring of the composition of the gas. This is achieved by using a quadrupole mass spectrometer (5) linked to a multi-port valve (4) with capillary tubes running to various

locations in the gas circuit. In a scanning mode, the mass spectrometer is able to determine precisely the mixing ratio of the three working gases, as well as to detect various contaminants.

The gas pressure in the RPCs and the recirculation circuit is chosen to be slightly higher than atmospheric pressure, to avoid contamination of the detector gas with air. Due to inevitable leaks, this also means that a small amount of fresh gas must be supplied continuously through the injection branch (6), where the total flow and composition of fresh gas is adjusted to be introduced into the main circuit at point E.

To clean the gas, e.g. during filling of the detector system, the gas can be collected by condensation (in 2). Contaminated gas runs into one of the two condenser units (path: ABG), while the other unit releases the gas into the main circuit again (path: HCDEF). All three gas species used in RPCs condensate before nitrogen and oxygen do, meaning that several cleaning cycles can be used to remove all air from the detector.

With the injection branch (6) existing already, it is foreseen to build a pilot system consisting of a circulation pump and mass spectrometer, and to investigate the gas composition on-line with a working RPC.

References

[1] R³B technical proposal; <http://www-land.gsi.de/r3b>

Acknowledgements

This work was financially supported by BMBF grant 06MZ222I.

The $\text{Ni}(\gamma, n)$ cross section: a benchmark for the s287 experiment*

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A systematic investigation of Coulomb excitation of neutron-rich nickel isotopes has been carried out at the LAND/R³B setup in Cave C at GSI. Beams of stable and unstable nickel isotopes at approximately 500 AMeV have been produced using fragmentation of ^{58}Ni and ^{86}Kr beams on a thick Be target and subsequent separation in the FRagment Separator (FRS). To study electromagnetic excitation, lead and carbon targets were used, in order to disentangle the electromagnetic and nuclear contributions. Tracking of the heavy fragments has been performed using position-sensitive pin diodes, scintillating glass fiber detectors and a time-of-flight wall of plastic scintillator paddles. Gammas were detected using a CsI scintillation detector in barrel geometry. Since mainly neutron-rich nuclei were under investigation, high-energy neutrons have been detected with the Large Area Neutron Detector (LAND), located at 0° and 15 m distance from the target.

Considering the nickel isotopes that have been measured during this experiment, a comparison with published data is possible for ^{58}Ni . Fultz *et al.* [1] provide photoneutron cross-sections, which may be converted to Coulomb excitation cross-sections using the Weizsäcker-Williams virtual photon approach for the given beam energy of 500 AMeV. For ^{58}Ni , Fultz *et al.* provide an inclusive photoneutron cross-section, leading in our case to the evaluation of not only the (γ, n) reaction channel, but also the (γ, np) channel. After folding the published cross-section with the virtual photon spectrum, an integral value of 127 ± 12 mb is obtained. Considering the data measured in the s287 experiment, the differential cross-sections for the (γ, n) and (γ, np) channels are shown in figure 1. Integrating these distributions provides cross-sections that need to be corrected for acceptance and efficiency of LAND.

The correct interpretation of the experimental data relies on simulations of the neutron detector. Figure 2 shows the dependence of the LAND acceptance and efficiency as a function of neutron kinetic energy in the rest frame. The acceptance remains at 100% up to 3.07 MeV and then decreases exponentially; its shape is determined by the geometry of the experimental setup. The total LAND efficiency is divided into a nominal and a calculated part. The nominal efficiency of 94% is equal to the intrinsic neutron detection efficiency of LAND for 500 MeV neutrons. This efficiency has been measured in a calibration experiment using neutrons at various energies, including 500 MeV. The calculated efficiency depends on experiment-specific detector effects, *e.g.* individual energy thresholds and inactive LAND subunits. Since the latter are not homogeneously distributed over the detector volume, position-dependent, and

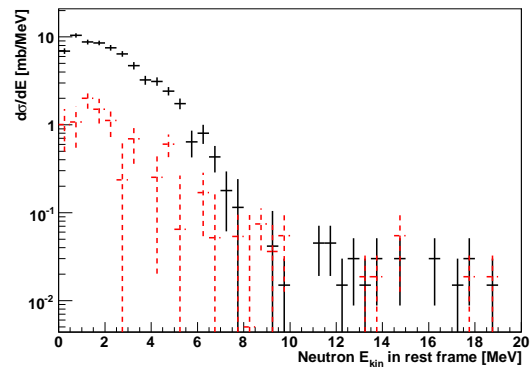


Figure 1: Differential cross section for $^{58}\text{Ni}(\gamma, n)$ (solid black lines) and $^{58}\text{Ni}(\gamma, np)$ (dashed red lines).

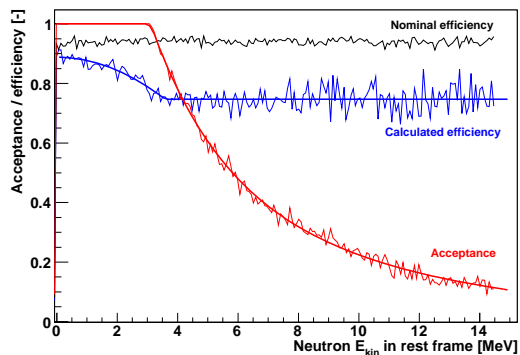


Figure 2: Neutron kinetic energy dependence of the LAND acceptance and efficiency.

therefore energy-dependent effects arise. The calculated efficiency is well described by a second-order polynomial up to 3.58 MeV (starting at 88.8%), and by a constant value of 74.7% from that energy upwards.

Based on this information, the measured cross-sections (for neutron energies up to 20 MeV) are corrected to 98 ± 2 mb and 9.9 ± 1.6 mb for the (γ, n) and (γ, np) channels respectively. Taking into account a systematic error of 6% on the efficiency, the resulting Coulomb excitation cross-section is 108 ± 10 mb, which is within agreement with the value provided by [1].

References

- [1] S. C. Fultz *et al.*, Phys. Rev. C **10**, 608 (1974)

*This work is supported in part by BMBF grant 06MZ2221.

Gettering of silicon by HCl gas

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Purpose of the work: In standard silicon solar modules, the costs of silicon wafers amounts up to 50% of the total costs. The reason is mainly the high costs for semiconductor quality wafers, as the purification steps are time and resource consuming. In order to save material costs, much research towards low - quality solar grade silicon and purification processes is made. Another approach is to use the concept of a crystalline silicon thin film (cSiTF) solar cell. Only a small amount of the expensive high purity silicon is needed for the epitaxial deposition on a substrate of metallurgical grade silicon (mg-Si). The resulting product is called epitaxial wafer equivalent (EpiWE) because it can be processed in a standard wafer cell production.

However, the metallurgical silicon used as substrate has a very high amount of doping and metallic impurities such as Fe, Cu, and Au. These contaminations severely degrade the minority carrier lifetime by forming recombination centres [1]. Therefore, the amount of impurities has to be reduced in order to prevent diffusion to the active layer. Since unidirectional solidification of the ingot cannot reach the appropriate impurity level, an effective gettering method is considered to be the following step.

Approach: Gettering of metal contaminations by HCl is known in the microelectronics during oxidation of wafers. The gettering effect is suggested to base on the formation of volatile metallic chloride species. The approach followed in this work is to treat the metallurgical silicon substrate by HCl gas, in the same CVD reactor prior to the deposition of high-purity silicon. The gettering mechanism as well as the reduction of the metal concentration is investigated in detail. For the analysis of metallic impurities, we apply standard analysis techniques like Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), and Instrumental Neutron Activation Analysis (INAA). The achievement of the gettering is controlled by comparing the amounts of trace elements before and after the gettering process. Using Fourier Transformed Infrared Spectroscopy (FTIR) we are able to investigate the exhaust gas and its components during the gettering process to optimize the method.

Scientific innovation and relevance: Gettering by HCl gas diluted in hydrogen is a new technique with promising results to reduce the metal contents. It enables in-situ processes, and by combining HCl gettering with HCl texture and emitter epitaxy, it seems to be possible to establish a fully dry in-line process for the wafer-equivalents. Neutron Activation Analysis shows to be a suitable measurement tool, which will be investigated for spatially resolved measurements and higher throughput.

Results: Gettering of the substrates was investigated on lowly contaminated multicrystalline and metallurgical silicon wafers. Lifetime measurements were performed, showing clearly the gettering effect by HCl gas. Gettering at 850°C with HCl concentrations between 5 and 16% shows a clear decrease of the total interstitial iron concentration of more than two orders of magnitude [2]. Lifetimes as high as the reference wafers, which were treated with the higher established method of phosphorus gettering, could be reached.

On metallurgical silicon, a decrease of the impurity concentrations was detected by Neutron Activation Analysis. This method was successfully developed for the detection of relevant impurities for solar cells. Microscopic examinations show that surface clusters are preferentially etched by HCl gettering, resulting in holes in the wafers.

Figure 1 shows the concentrations of several transition metals in mg-Si measured by NAA. The samples were taken from the top, middle and bottom of the silicon ingot, which was obtained by unidirectional solidification. An increase of the impurities from the bottom to the top is noticeable due to the small segregation coefficients of the respective metals in liquid and solid silicon.

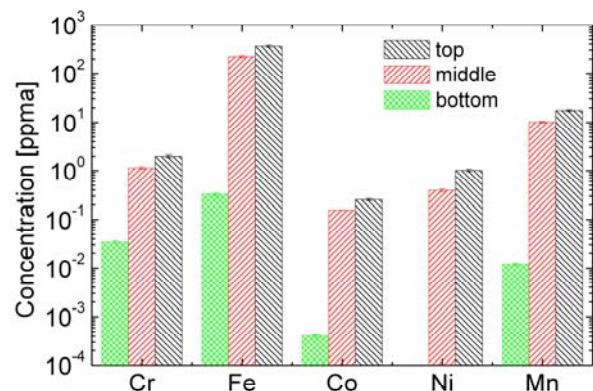


Figure 1. Impurity concentrations measured by NAA as they depend on the wafer position in the crystallised silicon ingot

Conclusions: HCl gas gettering shows promising results on multicrystalline and metallurgical grade silicon by decreasing the amount of impurities dramatically. The NAA method will be optimized for the routine application in photovoltaics.

References

- [1] Götzberger A, Voß B, Knobloch J. Sonnenenergie: Photovoltaik, Stuttgart, Teubner, 1993
- [2] Schmich E, Dissertation: High-temperature CVD processes for crystalline silicon thin-film and wafer solar cells, Freiburg, 2008

Separation and purification of no carrier added arsenic from bulk amounts of germanium being adequate to radiopharmaceutical labeling chemistry.

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Introduction: The element arsenic is well known as the favorite poison of the Savellis, the Borgias and Agatha Christie [1]. Another application of arsenic radioisotopes might be its use as radioactive probe in sub-toxic trace amounts for biological or medical purposes. The tracer concept of radiopharmaceutical chemistry allows the application of no carrier added (nca) amounts of radioactive isotopes (e.g. of arsenic) that are used for labeling of interesting biological carriers like monoclonal antibodies (mab) and the imaging of their biological behavior *in vivo*.

Experimental: Dissolving the target: The germanium target (100-200 mg) was placed in a quartz distillation apparatus (Fig. 1) and 4 ml *aqua regia* was added. The apparatus was heated to 120°C and during this time the irradiated germanium metal dissolved.

Distillation of GeCl₄: After complete dissolution of the target the temperature was maintained at 120°C for the distillation (Fig. 1) of GeCl₄. For acceleration of this process a stream of Argon was bubbled through the solution. Over a period of 1.5 h additional 6 ml of HCl (10 M) were added. After completed clearance the solution was condensed to less than 500 µl.

Anion exchange: The distillation solution was filled to 500 µl with 10 M HCl. The solution was transferred onto an anion exchange column (3*100 mm, AG1X8) in the chloride form and eluted with 500 µl fractions of 10 M HCl. Arsenic *As(V) was eluted in the fractions 2 and 3 (Fig. 2). After 10 fractions the eluent was switched to 0.1 M HCl for removal of gallium, germanium and zinc isotopes.

Reduction of As(V) to As(III), extraction into CCl₄ and back extraction into PBS-buffer: Fractions 2 and 3 were combined (1 ml solution) and mixed with 50 mg CuCl. The mixture was heated at 60 °C for different periods ranging from 5 to 120 minutes, with 60 minutes finally applied for the batch experiments. The As(III) was extracted twice with 500 µl CCl₄. Combined CCl₄ fractions were extracted with 500 µl PBS-buffer containing 25 mM EDTA and 0.5 M hydroxylamine.

Speciation of As(III) and As(V)

One of the key steps for labeling of mab with arsenic isotopes is the availability of *As(III) in the labeling solution. Care should be taken that the separated samples are used for labeling immediately or stored frozen in an atmosphere of argon to prevent the *As(III) from re-oxidation. The final fraction in 500 µl PBS contained > 95 % *As(III).

Labeling of Bevacizumab: The 500 µl of the purified radioarsenic solution in the PBS fraction was combined with 500 µl of Bevacizumab solution (1.25 mg, 8 nmol). 10 µl of TCEP (10 mg/ml, 420 nmol) were added and

the mixture was allowed to stand at room temperature for 1 h.

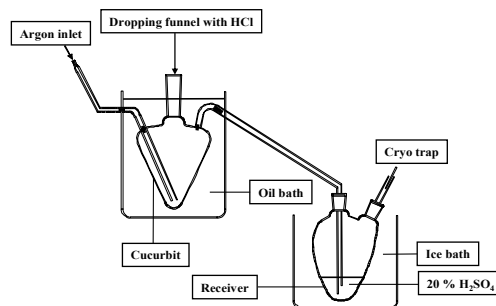


Figure 1. Schematic drawing of distillation apparatus

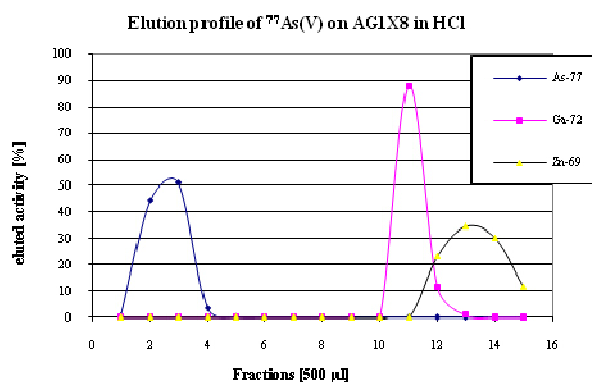


Figure 2. Elution profile of ⁷⁷As(V) distillate for reactor irradiated Ge target.

Results: Metallic germanium and ⁷⁷As(V) were first separated by distillation with an average separation factor of 2*10⁴. This was followed by purification with anion exchange chromatography for separation of the remaining germanium and radioactive trace amounts of ^{69m}Zn and ⁷²Ga formed during irradiation. The overall separation for germanium/arsenic was > 1*10⁶. The overall yield of *As(III) from the target to the final 500 µl PBS fraction was > 40%. Labeling of antibodies was successfully exemplified with the monoclonal antibody Bevacizumab providing labeling yields of > 99 % after 1 h incubation at room temperature.

References

[1] Zhu, J., et al., *How acute promyelocytic leukaemia revived arsenic*. Nat Rev Cancer, 2002. 2(9): p. 705-13.

Acknowledgement

This project was financially supported by DFG grant Ro 985 / 17.

Post-processing of $^{44}\text{Ti}/^{44}\text{Sc}$ radionuclide-generator for medical application

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Introduction: The $^{44}\text{Ti}/^{44}\text{Sc}$ generator provides cyclotron-independent access to positron-emitting ^{44}Sc for application in PET radiopharmaceuticals. The ^{44}Sc solution that can be obtained from generator is too diluted and too acidic for use in direct labeling procedures. The aim of this work was to design and to analyse the performance of a $^{44}\text{Ti}/^{44}\text{Sc}$ radionuclide generator for medical application.

Experimental: Post-elution processing studies were performed to reduce the volume and acidity of ^{44}Sc -eluate from $^{44}\text{Ti}/^{44}\text{Sc}$ generator and to reduce amount of ^{44}Ti in the final product for the syntheses of ^{44}Sc -labelled radiopharmaceuticals. It was developed, similar to the one developed for the $^{68}\text{Ge}/^{68}\text{Ga}$ radionuclide generator [1].

The $^{44}\text{Ti}/^{44}\text{Sc}$ generator was eluted with 20 ml mixture of 0.005 M $\text{H}_2\text{C}_2\text{O}_4/0.07$ M HCl. The retention of the ^{44}Sc eluate was checked on micro-chromatography columns, filled with 80 mg of cation-exchange resin AG W50x8 (200-400 mesh, H^+ -form). The columns were dried by passing air through them to remove the rest of eluate, then washed by 3 ml H_2O and dried once again. Several solutions at various volumes and concentrations were used to elute ^{44}Sc from the columns.

Finally micro-chromatography column (~2 mm inner diameter, ~5 mm length) was prepared using two 3-way valves filled with 53 mg of cationit. The $^{44}\text{Ti}/^{44}\text{Sc}$ radionuclide generator was connected to the valves via tubing. The ^{44}Sc -eluate mixture was transferred on-line within 20 min through the column. Subsequently, the column was washed by 3 ml H_2O and dried by air. Then, 3 ml of 0.25 M ammonium acetate, acidified to pH = 4.0 by drop-wise addition of acetic acid were passed slowly through the column and the ^{44}Sc eluate was collected in a 10 ml glass vial.

The aliquots of consecutive fractions were collected and measured according to the activity of ^{44}Sc and ^{44}Ti using dose calibrator and γ -spectroscopy.

Results: To reduce the volume of the ^{44}Sc eluate, a 3-valves cartridge with 53 mg of cationic resin AG W50x8 was connected with the generator on-line. Recently, the eluate passes through the cartridge and ^{44}Sc is adsorbed on the cationic resin, from which it can be eluted by 3 ml of 0.25 M ammonium acetate, pH=4.0. This solution is ready for labelling with peptides and other biomolecules. Finally, the cartridge is reconditioned by washing with 1 ml of 4 M HCl and 1 ml of water. The scheme of the generator together with post-elution processing is presented on Figure 1.

Conclusions: On-line post-elution processing of $^{44}\text{Ti}/^{44}\text{Sc}$ -radionuclide generator is performed on the small cationic

cartridge. In the final point, around 160 MBq of ^{44}Sc is obtained daily in 3 ml 0.25 M ammonium acetate buffer (pH=4.0). This solution can be used for labeling of biomolecules.

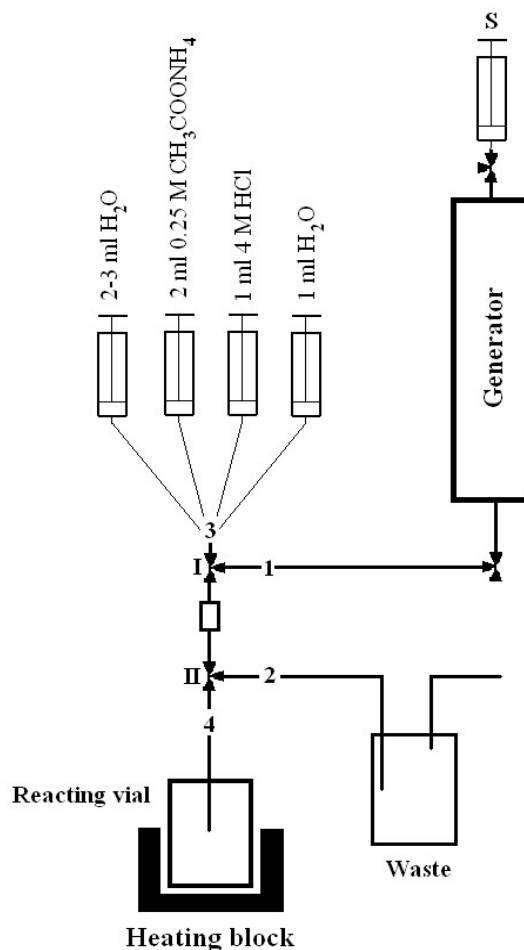


Figure 1. Scheme of the $^{44}\text{Ti}/^{44}\text{Sc}$ generator together with post-elution processing of ^{44}Sc -eluates and generator-associated syntheses of ^{44}Sc -labeled compounds.

References:

[1] K.P. Zhernosekov, D.V. Filosofov, R.P. Baum, P. Aschoff, H. Bihl, A.A. Razbash, M. Jahn, M. Jennewein, F. Roesch, Processing of generator-produced ^{68}Ga for medical application, *J. Nucl. Med.* (2007), 48, 1741 – 1748.

Acknowledgement:

This work was financially supported by DFG grant RO 985/18.

Labeling and stability studies of ^{44}Sc -DOTATOC

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Introduction: The radioisotope ^{44}Sc is a positron emitter, which is of interest for medical imaging using PET radiopharmaceuticals because of its 3.93 h half-life and 94% β^+ branching. The aim of this work was to find the optimum conditions for labeling a DOTA-conjugated octreotide (DOTATOC) with ^{44}Sc and to check the stability of obtained conjugate.

Experimental: The ^{44}Sc was eluted from the recently developed $^{44}\text{Ti}/^{44}\text{Sc}$ generator and on-line post-processed on the AG 50W-X8 resin [1]. Finally around 160 MBq ^{44}Sc was obtained in 3 ml of 0.25 M ammonium acetate buffer, pH = 4.0. This solution was used for labeling of DOTATOC directly. Optimisation of the reaction conditions was performed varying period and temperature of heating, addition of various amounts of DOTATOC and pH of the reaction mixture. The influence of microwave heating on the time and radiolabeling of DOTATOC with ^{44}Sc was determined under the optimal conditions found during the optimization experiments. Radiochemical analysis of ^{44}Sc -DOTATOC was accomplished using silica-coated TLC plates (Silica-gel 60) and 4 different developing solutions:

- 0.1 M sodium citrate pH = 4.0;
- 0.1 M sodium acetate pH = 4.0
- 5 % NaCl / MeOH (3:1);
- 5 % NaCl / MeOH / 25 % NH_3 (3:1:1).

^{44}Sc -DOTATOC was purified on a C-18 cartridge and eluted with 400 μl of pure ethanol. Stability of ^{44}Sc -DOTATOC was checked at room temperature and at 37 °C in EtOH, 0.9 % NaCl, PBS (pH=7.4) and in the presence of the metal cations Fe^{3+} , Ca^{2+} , Mg^{2+} and Cu^{2+} at 10^{-2} M concentration. The purified ^{44}Sc -peptide was diluted at least 20 times by the solution in which stability was checked.

Results: The overall radiolabeling yield was >96 % when 30 μl (21.1 nmol) of DOTATOC was added to 3 ml of the ^{44}Sc eluate (pH = 4.0) and heated in the oil-bath for 25 minutes at 95 °C. Changing the pH below 3 or increasing to > 5 resulted in a drop of labeling yield. Microwave-assisted labeling speeded up ^{44}Sc complexation with DOTATOC. After 1 minute of microwave heating reaction, the yield was >95 % and increased up to 98 % during next 2 min. Purification on the 30 mg C-18 cartridge recovered the ^{44}Sc -conjugate in 400 μl of pure EtOH with the radiochemical purity higher than 99 %.

Stability studies of about 160 MBq ^{44}Sc -DOTATOC in 400 μl of EtOH showed high stability of the labeled conjugate during at least 7 h. ^{44}Sc -DOTATOC was also stable during 8 h studies in 0.9 % NaCl and PBS at 37 °C. The obtained ^{44}Sc -DOTATOC seems to be kinetically very inert. It was stable even after 25 h incubation at 37 °C in the presence of metal cations at concentration 10^{-2} M.

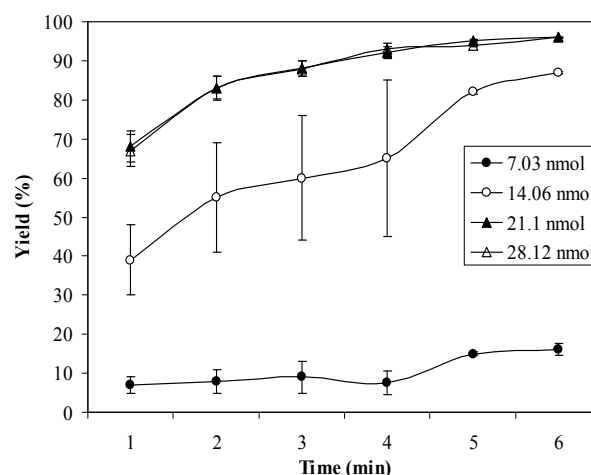


Figure 1. The labeling yield of ^{44}Sc -DOTATOC at 95 °C.

Conclusions: Optimum labeling of DOTATOC with ^{44}Sc in >96 % yield were obtained for 24.5 nmol of DOTATOC and 3 ml of ^{44}Sc eluate at pH = 4.0. The studies show high stability of the obtained ^{44}Sc -DOTATOC conjugate in different media. The potential diagnostic radiopharmaceutical was obtained after purification with more than 99% radiochemical purity. After membrane sterilization and dilution in saline it is ready for further cell and animal studies.

References:

- [1] N. Loktionova, D.V. Filosofov, M. Pruszyński, F. Rösch, Post-processing of $^{44}\text{Ti}/^{44}\text{Sc}$ -radionuclide-generator for medical application, 2008

Acknowledgement:

This work was financially supported by DFG grant RO 985/18.

Modification of the thermal column of the TRIGA Mainz for the treatment of liver metastases

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In 2001 the BNCT method was successfully applied for the extracorporeal treatment of liver metastases at the University of Pavia [1]. Due to this promising result the BNCT project shall be established at the University of Mainz in a close collaboration with the University of Pavia.

The requirements for the therapy in Mainz are ideal: Like the TRIGA reactors in Finland (Espoo) and Italy (Pavia), the TRIGA Mainz is well suited for BNCT. Its irradiation facility is easily accessible, there is sufficient flexibility concerning irradiation times and it is located close to the University Hospital. Nevertheless, medical and technical requirements as well as the legal regulations must be considered. In order to determine the optimal parameters for the planned therapy and for the design of the thermal column calculations were carried out using the MCNP-code as well as the transport

code ATTILA [2]. On the basis of the calculations, the reconstruction of the thermal column will be undertaken.

The irradiation facility must provide a homogenous thermal neutron field over the organ and a negligible gamma field at the irradiation position. To guarantee constant irradiation conditions in the thermal column during the treatment, online monitoring of the gamma and neutron component is desirable. The irradiation, handling and transport time for the explanted liver must be as short as possible. To maintain the organ in adequate extracorporeal conditions during the irradiation time, a special confinement which allows the placement of the organ in the thermal column and ensures storage of about 4 °C during the irradiation must be designed.



Fig.2: Planned modification of the irradiation channel of the thermal column. The image shows the transportation system for the organ, the gamma shielding is not included in the picture

At present, the accessible irradiation channel inside the thermal column has the size of 10 x 10 x 120 cm³, which is too small for the irradiation of a human liver. The channel is to be enlarged on a space of 30 x 30 cm². Furthermore, the optimum neutron flux for the liver can only be achieved in case the irradiation channel is lengthened, too. So far, two possible configurations have been discussed for the irradiation of the liver, one of which is displayed in fig. 2. The organ will be transported into the channel with a remotely controlled sleigh. The configurations differ in the irradiation position of the organ: Either 60 cm or 92 cm in distance to the core. Whereas

a distance 60 cm would be ideal, a distance of 92 cm is easier to construct. In this case, the neutron field is very favourable as well.

References:

[1] Pinelli et al. "TAOrMINA: From the First Idea to the Application to the Human Liver". Proceedings of the 10th International Congress on Neutron Capture Therapy, Monduzzi editore, Bologna, 2002, 1065-1072

[2] B. Wortmann "Auslegung und Optimierung einer Bestrahlungseinrichtung für die Bor-Neutroneneingangstherapie an autotransplantierten Organen", Dissertation, Technische Universität Dresden, Juni 2007

Determination of Boronophenylalanin (BPA) in healthy liver and tumour tissue of patients with liver metastases of colorectal carcinoma

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Patients suffering of colorectal carcinoma develop distant metastases in 50 to 80 % with the metastases being confined to the liver in almost half of those cases.

BNCT for patients with multiple, bilobar liver metastases was established at the University of Pavia with the first case being treated by Pinelli et al in Dec. 2001 [1]. Here, BPA was administered intravenously before explanting the liver and irradiation in the thermal column of the TRIGA-Reactor in Pavia. An accumulation of BPA in tumour vs. healthy liver tissue of 6:1 was determined here. Noteworthy is that the tissue samples were collected before explanting the liver.

The surgical process requires extensive experience in the field of liver transplantation and preservation of the liver during the extracorporeal treatment. This includes perfusion of the liver artery with preservation solution and reducing the liver temperature to 4°C. The question remains whether there are any wash-out effects during this procedure and if yes, will the accumulation remaining in tumour tissue still be enough for the irradiation therapy?

We plan to implement BNCT for colorectal liver metastases at the University of Mainz in cooperation with the University of Pavia.

Our project will be performed in two steps. The first step will be to determine the accumulation of BPA in tumour and healthy liver tissue in patients before and after partial liver resection and washing the liver specimen with preservation solution. Furthermore, additional pharmacokinetic data will be obtained from blood and urine samples taken in intervals during surgery. Satisfying results provided we would proceed with step 2 which is to treat a patient with multiple liver metastasis and extracorporeal irradiation of the whole liver.

We have started to examine the first samples of three patients. These patients suffer from colorectal liver metastases and they need a partial liver resection (fig.1). Our task is to determine the accumulation of BPA in tumour

and healthy liver tissue. BPA was administered in a concentration of 200 mg/kg intravenously, throughout the surgical procedure blood samples were taken every 30 minutes.

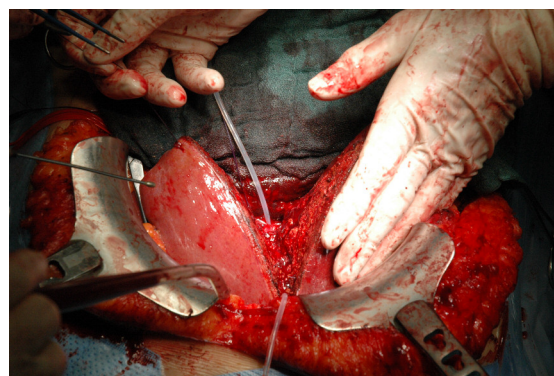


Fig.1: Resection of a liver lobe

After the resection of the liver, the specimen was perfused with preservation solution (250 ml through the artery and 1500 ml through the portal vein) and tissue samples were taken from the surface and depth of the organ to provide data for the spatial boron distribution. The samples were frozen in liquid nitrogen and prepared for analysis by the Department of Pathology by autoradiography and ICP-MS. In addition, the neutron and gamma dose was measured, using the liver specimen as matrix. Gold foils and thermo-luminescence detectors were fixed at different parts of the organ and irradiated in the thermal column. The analysis of the data is in progress. In case of an accumulation of BPA in tumour vs. healthy liver tissue of at least 3:1 in 3 patients we would proceed with the remaining 12 patients. The work on this project was kindly supported by the Boehringer Ingelheim Foundation

[1]: Pinelli et al. "TAORMINA: From the First Idea to the Application to the Human Liver". Research and Development in Neutron Capture Therapy. Proceedings of the 10th International Congress on Neutron Capture, Monduzzi editore, Bologna, 2002, 1065-1072

B.

**Radiopharmazeutische
Chemie / Kernchemie in den
Lebenswissenschaften**

**Radiopharmaceutical
Chemistry / Nuclear Chemistry
for Life Sciences**

Pharmacological characterisation of [¹⁸F]PR04.MZ and [¹¹C]PR04.MZ in papio Anubis baboons: A promising DAT-ligand for low-concentration imaging

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Introduction: The presynaptic dopamine transporter DAT has attracted a veritable interest due to its role in psychiatric and movement disorders. With respect to molecular imaging, cocaine derived, phenyltropanes have emerged as the most frequently considered imaging agents for this purpose. N-(4-fluorobut-2-yn-1-yl)-2β-carbomethoxy-3β-(4'-tolyl)nortropane (PR04.MZ) is a novel candidate for the non-invasive exploration of the neuronal dopamine transporter (DAT). It offers convenient labelling sites for both, carbon-11 to form [¹¹C]PR04.MZ and fluorine-18 [¹⁸F]PR04.MZ. We were interested in a comparative pharmacological characterisation of both tracers in papio anubis baboons.

Experimental: An adult female *papio anubis* baboon was studied using a test-retest protocol with [¹¹C]PR04.MZ and [¹⁸F]PR04.MZ. The injected doses ranged from 5.44 mCi to 0.51 mCi. Dynamic PET was conducted on a Siemens ECAT HR+ PET camera. Automated blood sampling was performed throughout the studies for plasma input and metabolite analysis. Metabolite-corrected plasma input functions were derived from the blood samples. The initial frames of the dynamic PET data were summed for coregistration with [¹⁸O]H₂O cerebral perfusion images and the obtained transformations (PET-PET) were used for coregistration of the individual dynamic PET data with the LONI-MR-atlas of the baboon brain. Regions of interest were drawn onto the anatomical MR-image and copied into the dynamic PET data. Time-activity curves and distribution volumes (DVs) were derived for the putamen, the caudate nucleus, the nucleus accumbens, the midbrain and the cerebellum. Distribution volumes (DV) for various brain regions were obtained from Logan-plot analysis and binding potentials were calculated according to the two compartment simplified-reference-tissue-model (SRTM). The test-retest reliability was calculated from the time activity curves for the specifically bound tracers.

Results: [¹¹C]PR04.MZ and [¹⁸F]PR04.MZ show a rapid, relatively high uptake into the DAT-containing brain regions inside and outside the striatum and low non-specific binding. Both the striatal as well as the extra-striatal DAT-populations are clearly visualised. Both tracers are rapidly metabolised, however, rodent studies did not indicate brain uptake of any metabolite.

Conclusion: In conclusion, PR04.MZ displays good test-retest reliability and visualises all DAT-containing brain regions in the primate brain. A long term scan with [¹⁸F]PR04.MZ showed reasonable washout after 90-120 min which is beneficial for the routine application of the

tracer in molecular diagnostics. The visualisation of the extra-striatal DAT in the midbrain might contribute to a more detailed, more sensitive exploration of neurodegenerative disorders with PET. Furthermore, the former facilitates the quantitative investigation of extrastriatal contributions to a variety of psychiatric diseases.

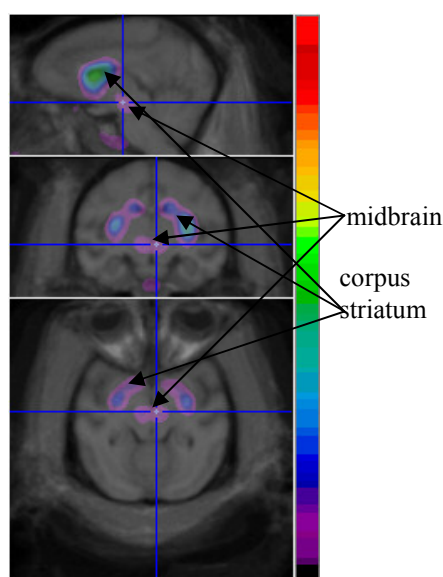


Figure 1: PET/MR-Fusion images of [¹¹C]PR04.MZ in a female papio anubis baboon

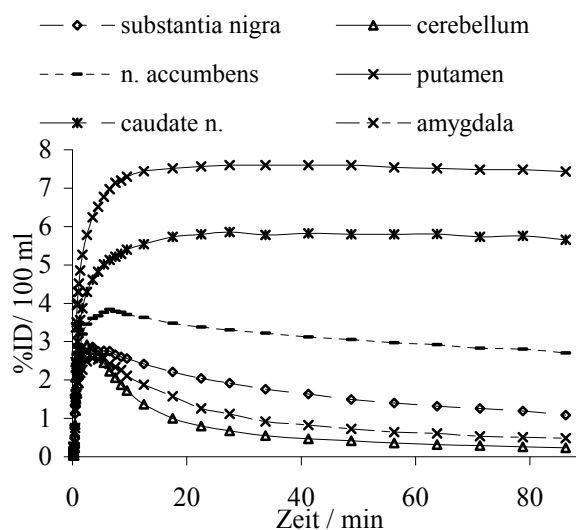


Figure 2: Time activity curves of various brain regions with [¹¹C]PR04.MZ in a female papio anubis baboon

Acknowledgement

The authors are grateful to the Fonds der chemischen Industrie. This work was supported by the DFG grant Ro 985/23

Synthesis and *in vitro* Affinities of Various MDL 100907 Derivatives as Potential ¹⁸F-Radioligands for 5-HT_{2A} Receptor Imaging with PET

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Objectives:

Radiolabelled piperidine derivatives such as [¹¹C]MDL 100907 and [¹⁸F]altanserin have played an important role in diagnosing malfunction in the serotonergic neurotransmission. Concerning molecular imaging, the advantage of [¹⁸F]altanserin (**b**) over [¹¹C]MDL 100907 (**a**) is the possibility to perform equilibrium scans lasting several hours and to transport the tracer to other facilities based on the 110 minute half-life of ¹⁸F-fluorine. A drawback of [¹⁸F]altanserin is its rapid and extensive metabolism. Four metabolites are formed in humans that cross the blood-brain-barrier, whereas metabolites of [¹¹C]MDL 100907 do not enter the brain to any larger extent. The aim of this study was to synthesize a ligand combining the reported better selectivity and *in vivo* stability of MDL 100907 as compared to altanserin and the superior isotopic properties of an ¹⁸F-label as compared to an ¹¹C-label.^{1,2}

Methods:

A variety of novel piperidine MDL 100907 derivatives, possible to label with ¹⁸F-fluorine, were synthesized to improve molecular imaging properties of [¹¹C]MDL 100907. Their *in vitro* affinities to a broad spectrum of neuroreceptors and their lipophilicities were determined and compared to the clinically used reference compounds MDL 100907 and altanserin.

Results:

The novel compounds MA-1 and (R)-MH.MZ show K_i-values in the nanomolar range towards the 5-HT_{2A} receptor and insignificant binding to other 5-HT receptor subtypes or receptors. Interestingly, compounds MA-1, MH.MZ and (R)-MH.MZ provide a receptor selectivity profile similar to MDL 100907. These compounds could possibly be preferable antagonistic ¹⁸F-tracers for visualisation of the 5-HT_{2A} receptor status. Medium affine compounds (e.g. VK-1) were synthesized and have K_i values between 30 and 120 nM (table 1).

All promising compounds show logP values between 2 and 3, i.e.

within range of those for the established radiotracers altanserin and MDL 100907. The novel compounds MA-1 and (R)-MH.MZ thus appear to be promising high affine and selective tracers of ¹⁸F-labelled analogues for 5-HT_{2A} imaging with PET.³

Table 1. Receptor Binding Affinities of promising 5-HT_{2A} ligands

Verbindung	K _i [nM]
MH.MZ	9.00 ± 0.10
MDL 100907	2.10 ± 0.13
(R)-MH.MZ	0.72 ± 0.12
MA-1	3.24±1.23

Conclusion:

A series of novel MDL 100907 derivatives containing a fluorine atom were synthesized and evaluated for their *in vitro* behaviour. Structure-Activity Relationships (SAR) studies suggested that the tested compounds had affinities to the 5-HT_{2A} receptor in the nanomolar range.

References:

- ¹ Herth, M.M. et al. (2008); Total synthesis and evaluation of [¹⁸F]MHMZ, *Bioorg. Med. Chem. Lett.* 1515-1519
- ² Huang et al. (1999), An Efficient Synthesis of the Precursors of [¹¹C]MDL 100907 Labeled in Two Specific Positions, *J. Labelled Cpd.* 42: 949 – 957
- ³ Herth et al. (2009), Synthesis and *in vitro* affinities of various MDL 100907 derivatives as potential ¹⁸F-radioligands for 5-HT_{2A} imaging with PET, *Bioorg. Med. Chem.* (submitted)

Radiolabeling and evaluation of MDL 100,907 derivatives as potential ^{18}F -radioligands to determine changes in endogenous serotonin

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Objectives: PET ligands that are able to detect changes in the concentration of endogenous serotonin are a valuable tool to study the pathophysiology of depressions and the effects of its pharmacotherapies¹. The purpose of this study was to explore the effect of paroxetine-induced increased serotonin levels on the binding of the 5-HT_{2A} antagonist (R)-[^{18}F]MH.MZ and its nitroderivate (R)-[^{18}F]VK1.MZ.

Methods: The *in vitro*-affinity for the inactive fluoro-compound (R)-VK1.MZ was determined in a [^3H]MDL 100,907 binding assay (Tab 1).

Table 1: In vitro affinities of the synthesized ligand to the 5HT_{2A}-receptor

compound	K _i [nM]
(R)-MH.MZ	0.7
(R)-VK1.MZ	12

Both radioligands were labeled with ^{18}F by fluoroethylation of the corresponding phenolic precursors using 2-[^{18}F]fluoroethyltosylate² (Fig 1).

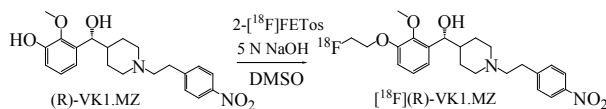


Figure 1: Radiosynthesis of (R)-[^{18}F]VK1.MZ

The radiolabeling procedure for (R)-[^{18}F]VK1.MZ was optimized due to time, temperature and solvent (Fig 2).

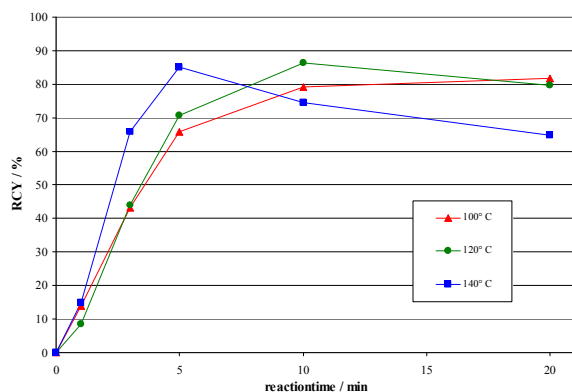


Figure 2: Radiosynthesis of [^{18}F](R)-VK1.MZ

Purification was carried out by HPLC and cartridge separation. Competition studies with serotonin were performed by autoradiography³ and a first μPET -study was carried out.

Results: Both ligands demonstrate good affinities in the nanomolar range and a high selectivity for the 5-HT_{2A} receptor. Optimization of the radiochemical reaction conditions for (R)-VK1.MZ gave radiochemical yields of about 85 % for the fluoroethylation after 5 minutes. The final formulation took no longer than 80 minutes and provided the labeled compound in a radiochemical yield of 50 % with a purity > 96 % and a typical specific activity of about 10 GBq/ μmol . Autoradiographic studies of (R)-[^{18}F]MH.MZ showed excellent binding properties (BP = 8.3), whereas (R)-[^{18}F]VK1.MZ showed a lower specific binding (BP = 2.4) (Fig 2). This is probably due to the decreased affinity. For both ligands the specific binding could be reduced significantly by the addition of 100 nM serotonin.

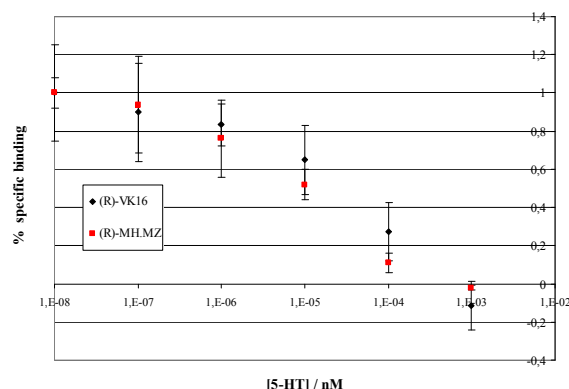


Figure 2: Competition study with serotonin

Conclusion: The reaction parameters for the radiolabeling of (R)-[^{18}F]VK1.MZ were optimized. (R)-[^{18}F]MH.MZ and (R)-[^{18}F]VK1.MZ could be obtained as an injectable solution in good radiochemical yields. Both tracers showed good binding properties *in vitro* and their specific binding could be reduced by the addition of physiological amounts of serotonin.

Outlook: μPET -studies with male rats under the influence of paroxetine are being performed in the close future using (R)-[^{18}F]MH.MZ due to its higher BP.

Literatur:

- [1] Giovacchini G, Lang L, Ma Y, Herscovitch P, Eckelman WC, Carson RE; (2005); Neuroimage 28, 238
- [2] Bauman A, Piel M, Schirmacher R, Rösch F; (2003); Tetrahedron Letters 44/51, 9165
- [3] Herth MM, Debus F, Piel M, Palner M, Knudsen GM, Lüddens H, Rösch F; (2008); Bioorg. Med. Chem. Lett. 18, 1515

Functional analysis of P-glycoprotein using 5-HT_{2A} ligand [¹⁸F]MH.MZ

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Introduction:

[¹⁸F]altanserin is the most frequently used tracer to image the 5-HT_{2A} receptor status *in vivo*. However, [¹⁸F]altanserin is a P-gp substrate as reported by Palner et al.¹ and very similar in structure to [¹⁸F]MH.MZ, a very promising 5-HT_{2A} antagonistic tracer recently developed.² The objective of this study was to determine the influence of the receptor binding of [¹⁸F]MH.MZ regarding P-gp activity

Methods:

[¹⁸F]MH.MZ was applied as a putative substrate to measure changes in 5-HT_{2A} receptor binding in transgenic P-gp KO and wild-type mice. μ PET was used to study the uptake profile of [¹⁸F]MH.MZ in various brain areas. Brain to plasma concentrations of [¹⁸F]MH.MZ and MH.MZ were determined *ex vivo*.

Results:

Highest uptake of [¹⁸F]MH.MZ was identified in the frontal cortex and in regions that agree with 5-HT_{2A} receptor distribution.

Conclusion:

In summary, the brain to plasma concentration ratios was higher in P-gp KO transgenic mice treated with MH.MZ vs. wild-type mice. Imaging studies provide evidence for the use of [¹⁸F]MH.MZ as a tool to measure not only changes in 5-HT_{2A} receptor density, but possibly in P-gp function, too.

References

- 1) Herth, Debus et al. (2008), Bioorg Med Chem Lett; 18:1515-1519
- 2) Palner et. Al (2007), Brain and Mind Forum, Abstracts)

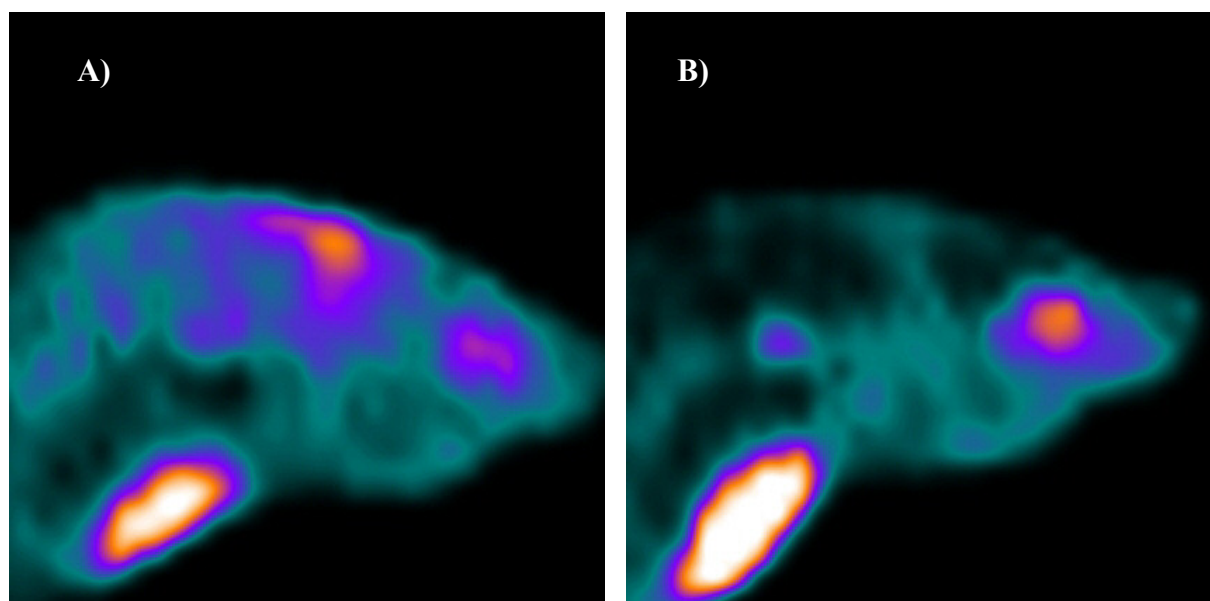


Fig. 1: [¹⁸F]MH.MZ PET scan of a A) P-gp k.o. and B) wild type mouse brain. Images derive from a 10 min. static scan 45 min. after i.p. injection of ~ 12 MBq. The imaging was performed with the Focus 120 microPET scanner

Synthesis and structure-activity-relationships of new 5-HT_{2A} receptor antagonists combining the structure of (R)-MH.MZ, altanserin and SR 46349B

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Objectives: ¹⁸F-labeled 4-benzoylpiperidine derivatives such as [¹⁸F]MH.MZ and [¹⁸F]altanserin play an important role as imaging agents to determine the 5-HT_{2A} receptor status *in vivo* using positron emission tomography (PET)¹. Both radioligands can be well accommodated to the binding model published by Anderson et al.². This binding model provides two possible directions in which 4-benzoylpiperidine derivatives can bind to the receptor binding site. The aim of this work was to develop new derivatives containing structure elements of both ligands, [¹⁸F]MH.MZ and [¹⁸F]altanserin, to clarify in which way they bind to the binding site. With this background it should be possible to deduce structures for new high affine ligands or to optimize established tracers.

Methods: Three new ligands were synthesised containing a 4-benzoylpiperidine moiety as lead structure. Therefore the phenolic hydroxylgroup of ketone (1) was deprotected and reacted with 1-brom-2-fluoroethane. The resulting compound (3) was deprotected and reduced with NaBH₄ to obtain the intermediate compounds (3a) and (3b) (Fig. 1).

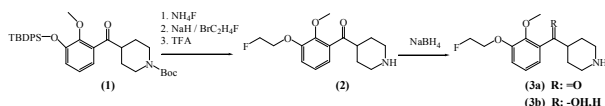


Figure 1: Synthesis of amine (3a) and (3b)

Reaction with boc-protected bromethylamine, deprotection and ringclosure with 2-thiocyanatobenzoic acid results in compounds (6a) and (6b) (Fig. 2).

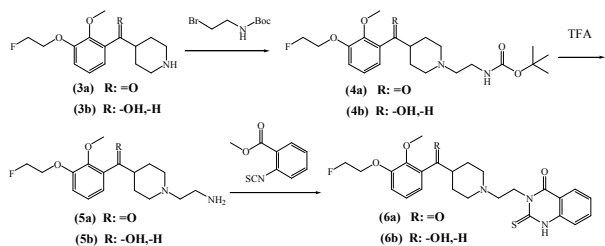


Figure 2: Synthesis of reference compounds (6a) and (6b)

For compound 6a the p-fluorophenyl ring of altanserin was replaced by the 3-fluoroethoxy-2-methoxyphenyl ring present in the structure of MH.MZ. Compound 6b contains a quinazolinone ring instead of the p-fluorophenyl substituent in the structure of MH.MZ. The O-dimethylaminoethyloxim residue present in the structure of SR 46349B, was introduced in compound 9 to study if it may improve its affinity (Fig 3).

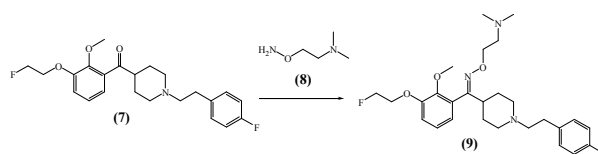


Figure 3: Synthesis of reference compound (9)

The *in vitro*-affinity for compounds (6a), (6b) and (9) was determined by a [³H]MDL 100,907 binding assay with GF-62 cells, expressing high amounts of the 5-HT_{2A} receptor.

Results: Altanserin binds to the 5-HT_{2A} receptor with the p-fluorobenzoyle moiety in a hydrophobic binding pocket and with a subnanomolar affinity. The remarkable reduced affinity of compound 1 and 2 indicates that the additional space required by the fluoroethoxy group and the methoxy group is not tolerated (Tab 1).

Table 1: Affinities to the 5-HT_{2A}-receptor

compound	K _i [nM]	compound	K _i [nM]
MH.MZ	9.03	(6a)	411
Altanserin	0.3	(6b)	390
SR46349B	1.3	(9)	57

These results demonstrate that [¹⁸F]MH.MZ can only bind to the 5-HT_{2A} receptor with the p-fluorophenylethyl residue in the hydrophobic binding pocket. By varying size and hydrophobic properties of the substituent in the para position it should be possible to improve the binding characteristics of the radioligand. The moderate affinity of compound (9) indicates that the O-dimethylaminoethyloxim residue requires to much additional space and lowers the affinity.

Conclusions: This work demonstrates that [¹⁸F]MH.MZ binds to the 5-HT_{2A} receptor with the p-fluorophenylethyl residue in a sterically restricted hydrophobic binding pocket. Structure-activity relationship (SAR) studies of derivatives with different p-substituents of [¹⁸F]MH.MZ were also performed³.

Literatur:

- [1] Herth MM, Debus F, Piel M, Palmer M, Knudsen GM, Lüddens H, Rösch F; (2008); Bioorg. Med. Chem. Lett. 18, 1515
- [2] Andersen K, Liljefors T, Gundertoft K, Perregaard J, Berges KP; (1994); J. Med. Chem. 37, 950
- [3] Herth MM, Kramer V, Piel M, Palmer M, Riss PJ, Knudsen GM, Rösch F, (2009); Bioorg. Med. Chem. (submitted)

Synthesis of novel WAY 100635 derivatives containing a norbornene group and radiofluorination of [¹⁸F]AH1.MZ, as a Serotonin 5-HT_{1A} Receptor Antagonist for molecular Imaging

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Introduction:

5-HT_{1A} receptors are involved in a variety of psychiatric disorders and *in vivo* molecular imaging of the 5-HT_{1A} status represents an important approach to analyze and to treat these disorders. Recently, Fiorino et al.¹ synthesized new arylpiperazines containing a norbornene group as 5-HT_{1A} receptor antagonists and reported their outstanding *in vitro* selectivity for the 5-HT_{1A} receptor. Therefore, we decided to slightly modify promising ligands by replacing a methoxy- by a fluoroethoxy group for labelling purposes, to alter the position of the fluoroethoxy group within the phenylic ring and to determine the affinities of the new compounds towards several 5-HT receptor subtypes. Also, we report the optimized labelling and purification procedure of the promising candidate [¹⁸F]AH1.MZ.

Methods:

Organic synthesis of WAY 100635 derivatives containing a norbornene group has been described by Fiorino et al.. Due to the necessary structural replacement of a methoxy- by a fluoroethoxy group for labelling purposes, a similar synthesis route was applied, but hydroxyphenylpiperazines were used as starting materials for both precursors and reference compounds. Moreover, the ¹⁸F-labelling was carried out similar to the one reported in Herth et al. (2008) and the *in vitro* receptor profile was provided by PDSP.

Results:

Three potential 5-HT_{1A} antagonists could be synthesized in total yields of 15%. *In vitro* affinities of the three compounds were in a low to moderate nanomolar range for AH1.MZ (1) ($K_i = 4.2$ nM) and AH2.MZ (2) ($K_i = 30$ nM), whereas AH3.MZ (3) shows no affinity towards the 5-HT_{1A} receptors (Figure 1). Moreover, AH1.MZ and AH2.MZ showed a reasonable *in vitro* affinity profile and should enable the imaging of the 5-HT_{1A} receptor by PET.

The [¹⁸F]fluoroalkylation was optimized only due to temperature variation resulting in radiochemical yields of > 70%. Final reaction conditions were 120 °C, 7 mmol precursor and 7 mmol 5 N NaOH

dissolved in 1 mL of dry DMSO with a reaction time of 20 minutes.

Conclusion:

Fiorino et al. reported about an outstanding high affinity ($K_i = 0.021$ nM) and selective compound. By replacing the methoxy- by a fluoroethoxy group of the parent compound, three different reference compounds (1)-(3) were obtained enabling a labeling strategy with [¹⁸F]FETos. *In vitro* evaluation of these ligands showed high to moderate affinities to the 5-HT_{1A} receptor for AH1.MZ and AH2.MZ, but no affinity of AH3.MZ toward the 5-HT_{1A} receptor of the p-substituted fluoroethylated compound. The receptor profile of AH1.MZ and AH2.MZ demonstrates selectivity within the 5-HT system. However, the outstanding affinity and selectivity of the literature reference compound is mainly lost by introducing a fluoroethyl group. Nevertheless, compounds AH1.MZ and AH2.MZ may provide potential for molecular imaging the 5-HT_{1A} receptor system. ¹⁸F-labelling via [¹⁸F]FETos was carried out and optimized up to RCY of > 70%.

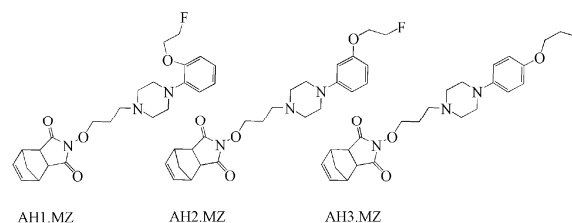


Figure 1: Structures of novel WAY 100635 derivatives

References:

¹Fiorino et al.; J. Med. Chem. 2005, 48, 5495-5503

Syntheses and biological evaluation of new compounds as potential imaging agents for the NMDA-receptor

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Introduction: The NMDA receptor plays a central role in several disorders in the CNS. To provide effective ligands for the glycine binding site for PET imaging, a new series of indole-2-carboxylate derivatives have been synthesized.

Experimental: Based on the indole-2-carboxylate GV150526 (1), a series of ethyl esters and free acids were synthesized, which are conjugated with a fluoroethoxy group in the terminal phenyl ring in ortho, meta and para position. These new compounds, namely ethyl-3-((E)-2-((2/3/4-fluoroethoxy)-phenylcarbamoyl)-vinyl)-4,6-dichloro-1H-indole-2-carboxylate (**1**, **3**, **5**) and the corresponding carboxylic acids (**2**, **4**, **6**) were synthesized, cf. Figure 1.

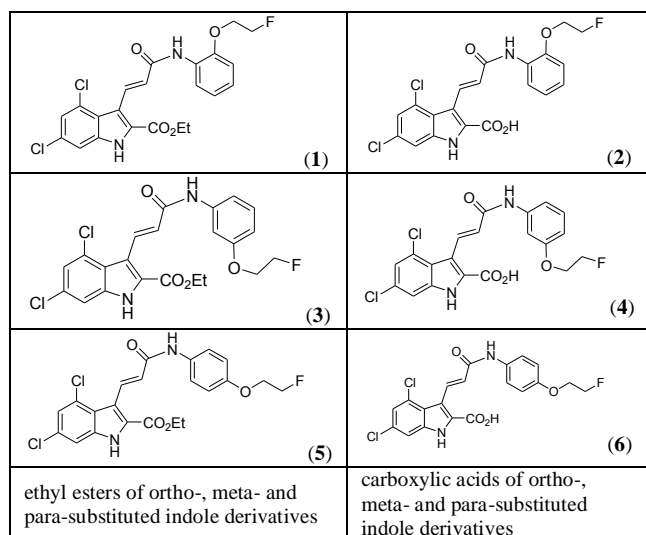


Figure 1. Structures of synthesized NMDA-ligands

Each target compounds can be synthesized in a 8 step reaction. The reaction scheme is shown in Figure 2. The IC₅₀ values of the ¹⁹F-inactive compounds were determined using a [³H]MDL-105,519 receptor binding assay [2].

The fluorine-18 labelled analogue of the most promising compound could be used for imaging the NMDA receptor by PET.

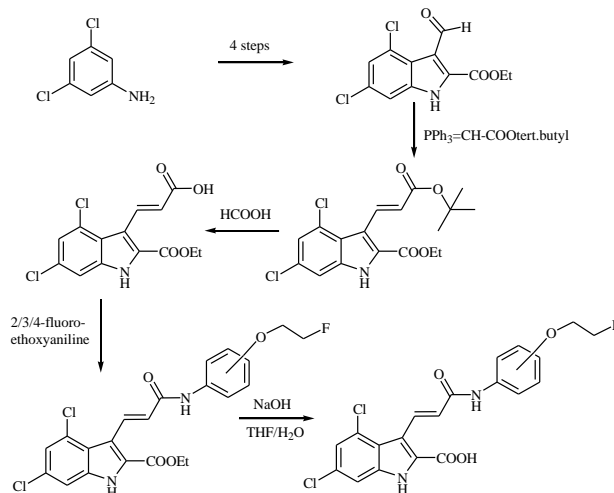


Figure 2. Reaction scheme for the inactive reference compounds

Results: The affinity data of the ethyl esters show affinities about 300 μM, c.f. Table 1. But the affinities improve dramatically for the free acids in the order ortho (1438 nM) > meta (595 nM) > para (0.23 nM) for the substitution of the terminal phenyl ring. The data demonstrate that affinity depends on the variation of the fluoroethoxy group. Especially the para substituted compound shows affinity in the low nanomolare range. The radiolabelled analogue could be used as imaging agent. Therefore the design of the precursor has to carry the phenolic hydroxyl group in para position. Hence the precursor could be labelled with [¹⁸F]fluoroethyltosylate. The synthesis of the precursor molecule for this promising compound is in process.

compound	substitution	IC ₅₀ / μmol
1	ortho-fluoroethoxy substituted ester	258,45
3	meta-fluoroethoxy substituted ester	276,54
5	para-fluoroethoxy substituted ester	401
2	ortho-fluoroethoxy substituted acid	1,438
4	meta-fluoroethoxy substituted acid	0,595
6	para-fluoroethoxy substituted acid	0,00023

Table 1. Affinity of the synthesized compounds

References

- [1] Di Fabio, R. et al.; J. Med. Chem. 1997, 40, 841-850
 [2] Jansen, M.; Potschka, H.; Brandt, C.; Löscher, W.; Dannhardt G.; J. Med. Chem. 2003, 46, 64-73

Acknowledgement

This work was financially supported by DFG grant RO 985/20-1.

Synthesis, biological evaluation and radiolabelling of a quinolin derivative as a potential imaging agent for the NMDA-receptor

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Introduction: The *N*-methyl-D-aspartate (NMDA) receptor is involved in the majority of neuroexcitatory events and important for neuronal development, functioning and degeneration in the CNS. Its adaptive properties and the presence of numerous regulatory sites could be the basis of its role in learning and memory as well as in neurodegenerative pathologies disorders such as M. Parkinson and Alzheimer's disease. Due to promising results [1] the synthesis of a 3-substituted 4-hydroxy-quinolin-2(1*H*)-one derivative was started, which can be labelled with 2-[¹⁸F]fluoroethyltosylate.

Experimental: For affinity determination, the inactive reference compound 7-chloro-3-[3-[4-(2-fluoro-ethoxy)-phenoxy]-phenyl]-4-hydroxy-1*H*-quinolin-2-one was synthesized in a nine step reaction. In parallel, the synthesis of the precursor was done. Radiolabelling was achieved on the terminal phenolic hydroxy group with 2-[¹⁸F]fluoroethyltosylate, c.f Figure 1.

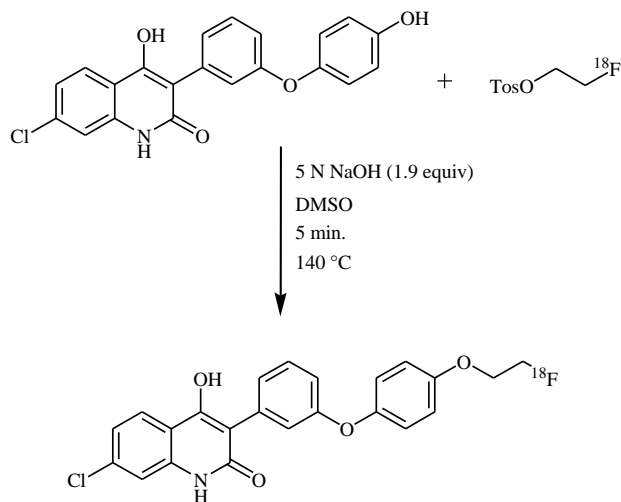


Figure 1. Radiosynthesis of the para-substituted fluoroethoxy-quinolin derivative

Different temperatures and precursor concentrations were used to optimize the reaction to get the desired compound in high radiochemical yields. After 1, 3, 5, 7, 10, 15 and 20 minutes aliquots (0.1 mL) of the reaction mixture were taken and quenched with water (0.1 mL). The reaction yield was determined with radio TLC. The findings of the optimization process are shown in Figure 2. The best results were obtained for 1 minute reaction time at 140 °C, 3 mg of precursor and DMSO as solvent. 2 μ L of a 5 N NaOH-solution (1,9 equiv) were used.

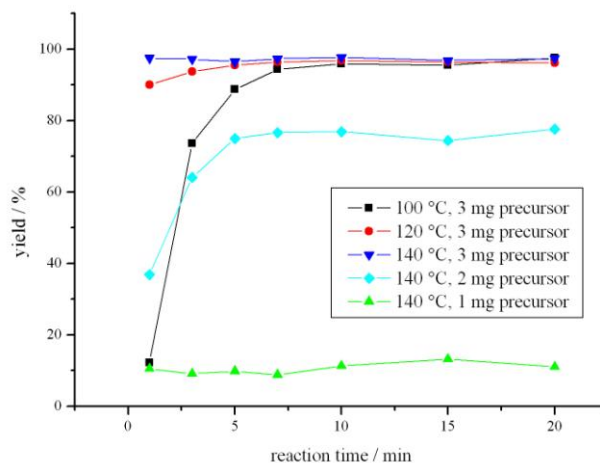


Figure 2. Results of the optimization process

To reduce the tailing effect of the precursor on the HPLC, only 2 mg were used. For separation, the whole reaction mixture was diluted with 1 mL of water and injected into a semipreparative HPLC system, equipped with a Luna PFP (250 x 10 mm) column. After successful separation, the HPLC effluent, containing the labelled compound was fixed on a strata-X cartridge and washed with water. The final compound was completely eluted by the use of ethanol (2.5 mL). Characterisation was done with radio TLC and analytical radio HPLC.

Results: Radiolabelling does succeed with > 95 % RCY within one minute at 140 °C and 3 mg of precursor concentration. For radiosynthesis and separation, 2 mg of precursor were used. Reaction time was extended to 5 minutes. The final product was analysed by analytical HPLC and radio TLC. Due to optimized and practicable reaction parameters, further experiments of the labelled compound are being planned. The log P value and has to be determined. Evaluation of the radioligand and animal studies on the micro PET are planned. The determination of the IC₅₀ values of the ¹⁹F-inactive compounds, using [³H]MDL-105,519 receptor binding assay [2] is ongoing.

References

- [1] Kreimeyer, A.; Laube, B.; Sturgess, M.; Goeldner, M.; Foucaud, B.; J. Med. Chem. 1999, 42, 4394-4404
- [2] Jansen, M.; Potschka, H.; Brandt, C.; Löscher, W.; Dannhardt G.; J. Med. Chem. 2003, 46, 64-73

Acknowledgement

This work was financially supported by DFG grant RO 985/20-1.

Synthese des Nitro-Markierungsvorläufers der Verbindung TC07

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Einleitung: γ -Aminobuttersäure (GABA) ist der primäre, inhibitorische Neurotransmitter im zentralen Nervensystem der Säugetiere und wechselwirkt mit dem GABA-Rezeptor. Insbesondere zeigte sich in den letzten Jahren, dass der Einfluss der Untereinheiten des GABA_A-Rezeptor in diversen Krankheitsbildern eine große Rolle spielt und deshalb immer mehr die einzelnen Untereinheiten im Mittelpunkt der aktuellen Forschung stehen. Die relativ hohe Häufigkeit von etwa 20% der α_5 -Untereinheit des GABA_A-Rezeptors im Hippocampus lässt die Vermutung zu, dass diese Untereinheit einbezogen ist in die Kontrolle von Emotionen und Ängsten, sowie in Lern- und Gedächtnisvorgängen. Dies macht sie besonders interessant im Bezug auf neue, diagnostisch und therapeutisch verwendbare Erkenntnisse über neurodegenerative Prozesse, in denen besonders die Gedächtnisfunktion und das Lernvermögen beeinträchtigt werden, wie z.B. Alzheimer und über Erkrankungen wie Autismus und posttraumatische Neurosen. Auf Basis der bereits synthetisierten Referenzverbindungen TC07-TC12 und deren ermittelter Affinitäten soll der Ligand TC07 ¹⁸F-markiert werden. Aufgrund ihrer guten Eigenschaften wurde die Nitrofunktion als Abgangsgruppe gewählt.

Experimentell: Zur Synthese des Nitro-MVs musste zunächst eine Struktur mit nukleofuger Gruppe synthetisiert werden. Dafür wurde ein literaturbeschriebener, fünfstufiger Syntheseweg gewählt (Abb. 1). Zunächst wurde die Amino-Funktion des 2-Amino-6-methylpyridins acetylgeschützt^[1] um dann in hoher Ausbeute mit Peressigsäure zum korrespondierenden N-Oxid (**34**) umgesetzt zu werden^[2]. Dieses wurde zur Bildung der späteren Abgangsgruppe zum 6-Nitro-2-methylpyridin-N-oxid (**35**) oxidiert. Als gängiges Oxidationsmittel wurde in der Literatur^[3,4] zur Bildung einer Nitrofunktion aus einer Aminofunktion stets Caro'sche Säure verwendet. Diese Reaktion stellte sich als extrem problematisch dar, da der Reaktionsverlauf sehr stark exotherm verlief und daher nur sehr schwer zu kontrollieren war. Für den weiteren Syntheseverlauf wurde zunächst das 6-Nitro-2-methylpyridin-N-oxid (**35**) durch Zugabe von Acetanhydrid zum 6-Nitro-2-acetoxymethylpyridin (**36**) umgesetzt wurde. Im Anschluss wurde alkalisch hydrolysiert und das gewünschte Endprodukt 6-Nitro-2-pyridinmethanol (**37**) in insgesamt sehr schlechter Ausbeute erhalten.

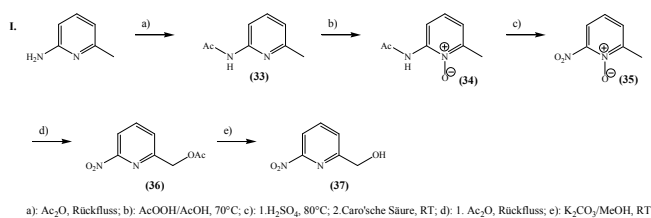


Abb. 1: Darstellung von 6-Nitro-2-pyridinmethanol nach Syntheschema I

Daher wurde ein modifizierter Syntheseweg über eine radikalische Substitution mit anschließender Hydrolyse verwendet (Schema II, siehe Abb. 2).

Zur Darstellung des dafür benötigten Ausgangsproduktes 6-Nitro-2-methylpyridin (**38**) konnte trotz der schwierigen Reaktionskontrolle und der schlechten Ausbeuten nicht auf eine Oxidation mit Caro'scher Säure verzichtet werden. Allerdings konnte diese Reaktion ausgehend von 6-Amino-2-methylpyridin ohne weitere Zwischenstufen durchgeführt werden und somit auch ohne großen synthetischen Aufwand 6-Nitro-2-methylpyridin (**38**) erhalten werden. Dieses wurde radikalisch mit N-Bromsuccinimid an der Methylgruppe einfach bromiert und anschließend alkalisch zur Hydroxyfunktion des 6-Nitro-2-pyridinmethanol (**37**) hydrolysiert.

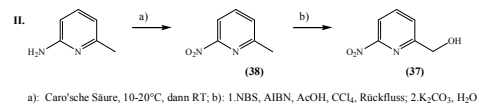


Abb. 2: Alternativer Syntheseweg nach Schema II

Die Darstellung des Nitro-MVs basiert primär auf der Deprotonierung des 6-Nitro-2-Pyridinmethanols und der nachfolgenden Kopplung durch Zugabe eines Grundkörpers B7. Die Synthese des Grundkörpers B7 wurde bereits in einem vorhergehenden Jahresbericht beschrieben^[5].

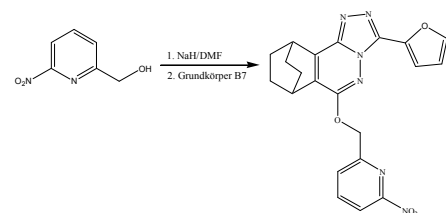


Abb. 3: Darstellung des Nitro-MVs

Ergebnisse: Die Synthese des Nitro-MV verlief mit vergleichsweise schlechten Ausbeuten. Besonders die Oxidation zur Nitro-Funktion stellte große synthetische Anforderungen.

Im Weiteren soll dieser Markierungsvorläufer mittels Hand-synthese und Mikrowellenreaktion unter verschiedenen Reaktionsbedingungen ¹⁸F-markiert werden.

Referenz:

- [1] Gannett P.M., Johnson E.M., Grimes M.A. et al., J Label Comp Radiopharm 46 (2003), 107-114
- [2] Adams R., Miyano S., J Am Chem Soc 76 (1954), 2785
- [3] Ashimori A., Ono T., Uchida T. et al., Chem Pharm Bull 38(9) (1990), 2446-2458
- [4] Brown E.V., J Am Chem Soc 79 (1957), 3565-3566
- [5] Capito T., Piel M., Rösch F., Jahresberichte 2007, Universität Mainz

Danksagung:

Diese Arbeit wurde finanziell unterstützt durch das Graduiertenkolleg 1044/1 „Entwicklungsabhängige und krankheitsinduzierte Modifikationen im Nervensystem“.

Synthese von [¹⁸F]TC07 über einen Nitro-Markierungsvorläufer

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Einleitung: γ -Aminobuttersäure (GABA) ist der primäre, inhibitorische Neurotransmitter im zentralen Nervensystem der Säugetiere und wechselwirkt mit dem GABA-Rezeptor. Insbesondere zeigte sich in den letzten Jahren, dass der Einfluss der Untereinheiten des GABA_A-Rezeptor in diversen Krankheitsbildern eine große Rolle spielt und deshalb immer mehr die einzelnen Untereinheiten im Mittelpunkt der aktuellen Forschung stehen. Die relativ hohe Häufigkeit von etwa 20% der α_5 -Untereinheit des GABA_A-Rezeptors im Hippocampus lässt die Vermutung zu, dass diese Untereinheit einbezogen ist in die Kontrolle von Emotionen und Ängsten, sowie in Lern- und Gedächtnisvorgängen. Dies macht sie besonders interessant im Bezug auf neue, diagnostisch und therapeutisch verwendbare Erkenntnisse über neurodegenerative Prozesse, in denen besonders die Gedächtnisfunktion und das Lernvermögen beeinträchtigt werden, wie z.B. Alzheimer und über Erkrankungen wie Autismus und posttraumatische Neurosen. Auf Basis der bereits synthetisierten Referenzverbindungen TC07-TC12 und deren ermittelter Affinitäten soll der Ligand TC07 ¹⁸F-markiert werden. Aufgrund ihrer guten Eigenschaften wurde die Nitrofunktion als Abgangsgruppe gewählt.

Experimentell: Es wurden alle dargestellten MV^[1,2] hinsichtlich ihrer Eignung zur Darstellung von [¹⁸F]TC07 untersucht. Dabei konnte festgestellt werden, dass sowohl der Chlor- als auch der Brom-MV aufgrund ihrer sehr schlechten radiochemischen Ausbeuten von unter 5 % nicht zur Darstellung von TC07 geeignet sind. Da der Nitro-MV sich in ersten Synthesen mit guten Ausbeuten umsetzen lässt, wurde die Synthese des [¹⁸F]TC07 ausgehend von einem Nitro-MV optimiert. Dabei wurden die Reaktionsparameter Reaktionszeit und -dauer, Temperatur, Lösungsmittel, Basenzusatz sowie Basen- und MV-Konzentration variiert. Ferner wurde die Reaktion sowohl im Ölbad als auch in der Mikrowelle (Powertest- und Standardmodus) durchgeführt. Exemplarisch seien hier zwei aufgenommene Kinetiken in Abhängigkeit von Reaktionstemperatur und -dauer (2,4 μ mol MV, DMF, K₂CO₃/K222; Abb. 1 und 2) gezeigt.

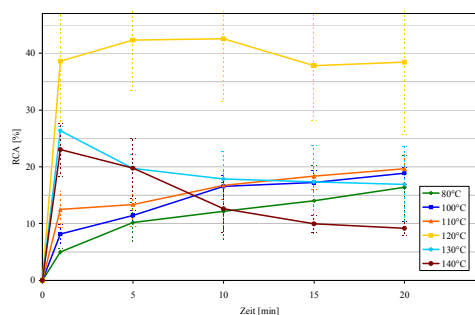


Abb. 1: RCA im Ölbad

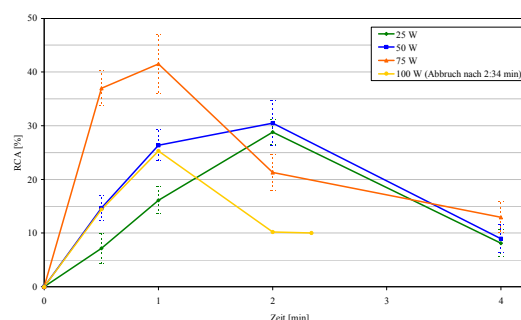


Abb. 2: RCA im Powertest-Modus der Mikrowelle

Im Anschluss an die Optimierung der Reaktion erfolgte die Abtrennung des [¹⁸F]TC07 und dessen Überführung in eine injizierbare Lösung. Dabei erfolgte die Separation des Radioliganden mittels semipräparativer HPLC (LiChrospher100 RP 18-5 μ EC, 10 ml/min, MeCN/0,1 M NaAc-Puffer 50/50).

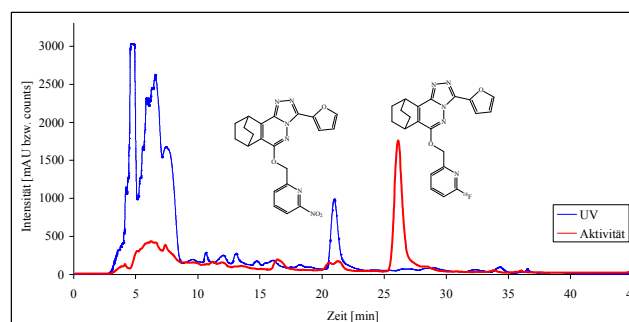


Abb. 3: HPLC-Abtrennung von [¹⁸F]TC07

Die so erhaltene Produktfraktion wurde auf einer C18-Kartusche fixiert, mit 2 ml Diethylether in einen Rundkolben überführt und das Lösungsmittel mittels eines Mini-Rotationsverdampfers im Vakuum entfernt. Der Produktkolben wurde mit isotonischer Kochsalzlösung versetzt, mit Ultraschall behandelt und in ein Eppendorffgefäß überführt.

Ergebnisse: Nach Optimierung der Reaktionsparameter konnte [¹⁸F]TC07 in guten radiochemischen Ausbeuten von über 40 % sowohl im Ölbad als auch in der Mikrowelle erhalten werden. Nach Überführung in eine injektionsfähige Lösung konnte eine korrigierte radiochemische Ausbeute von 15 % nach etwa 110 min ermittelt werden. Im Weiteren sollen die Evaluierung des ¹⁸F-markierten Liganden TC07 in Kooperation mit der psychiatrischen Klinik und Poliklinik erfolgen.

Referenz:

[1]Capito T., Piel M., Rösch F., Jahresberichte 2007, Universität Mainz
[1]Capito T., Rösch F., Jahresberichte 2008, Universität Mainz

Danksagung

Diese Arbeit wurde finanziell unterstützt durch das Graduiertenkolleg 1044/1 „Entwicklungsabhängige und krankheitsinduzierte Modifikationen im Nervensystem“.

Evaluierung des PET-Liganden [¹⁸F]TC07

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Einleitung: γ -Aminobuttersäure (GABA) ist der primäre, inhibitorische Neurotransmitter im zentralen Nervensystem der Säugetiere und wechselwirkt mit dem GABA-Rezeptor. Insbesondere zeigte sich in den letzten Jahren, dass der Einfluss der Untereinheiten des GABA_A-Rezeptor in diversen Krankheitsbildern eine große Rolle spielt und deshalb immer mehr die einzelnen Untereinheiten im Mittelpunkt der aktuellen Forschung stehen. Die relativ hohe Häufigkeit von etwa 20% der α_5 -Untereinheit des GABA_A-Rezeptors im Hippocampus lässt die Vermutung zu, dass diese Untereinheit einbezogen ist in die Kontrolle von Emotionen und Ängsten, sowie in Lern- und Gedächtnisvorgängen. Dies macht sie besonders interessant im Bezug auf neue, diagnostisch und therapeutisch verwendbare Erkenntnisse über neurodegenerative Prozesse, in denen besonders die Gedächtnisfunktion und das Lernvermögen beeinträchtigt werden, wie z.B. Alzheimer und über Erkrankungen wie Autismus und posttraumatische Neurosen. Auf Basis der bereits synthetisierten Referenzverbindungen TC07-TC12 und deren ermittelter Affinitäten soll der Ligand TC07 ¹⁸F-markiert werden. Aufgrund ihrer guten Eigenschaften wurde die Nitrofunktion als Abgangsgruppe gewählt.

Experimentell: Nachdem [¹⁸F]TC07 in eine injektionsfertige Lösung überführt werden konnte, sollte zunächst die Affinität und Selektivität dieses Liganden in Autoradiographien bestätigt werden. Dafür wurden wie auch schon in vorangegangenen Autoradiographien 14 μ m dicke, transversale Rattenhirnschnitte verwendet.

Es wurden für alle Hirnschnitte jeweils 3 nM [¹⁸F]TC07 verwendet. Die Verdrängung des Radioliganden erfolgte mit je 10 μ M des kalten TC07 (spezifische Bindung) und Zolpidem (unspezifische Bindung). Visuell ist hier keine Anreicherung in irgendeiner spezifischen Gehirnregion zu erkennen. Der Vergleich der Aktivitätsmengen in spezifischen Hirnregionen mit nachgewiesener hoher α_5 -Dichte zeigte keine spezifische Anreicherung. Grund hierfür ist die sehr hohe unspezifische Bindung des Radioliganden, die eine Auswertung der Daten nahezu unmöglich macht.

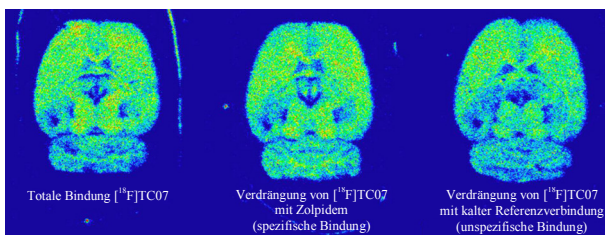


Abb. 1: Transversale Autoradiographien, A: totale Bindung, B: spezifische Bindung und C: unspezifische Bindung von je 3 nM [¹⁸F]TC07

Im Anschluß an die autoradiographischen Experimente wurden μ PET-Studien angeschlossen. Dafür wurde mit

Isofluran narkotisierten Sprague-Dawley Ratten der Radioligand [¹⁸F]TC07 appliziert. Es wurden dynamische Scans über einen Zeitraum von 60 min durchgeführt.

Während die Harderschen Drüsen gut zu erkennen sind, zeigt sich für das Gehirn keine signifikante Anreicherung des Radioliganden.

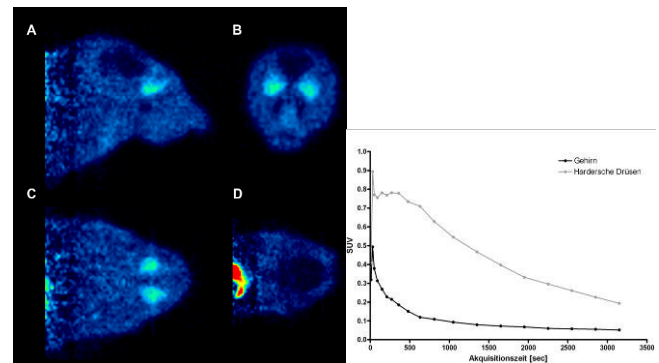


Abb. 2: Links: PET-Bilder von [¹⁸F]TC07; A sagital, B coronal, C transversal, jeweils auf Höhe der Harderschen Drüsen und D transversal auf Höhe des Gehirnes. Rechts: Repräsentative Zeit-Aktivität-Kurve der PET-Aufnahme.

Die Resultate der aufgenommenen Zeit-Aktivitäts-Kurve zeigen im Gehirn eine maximale Aufnahme von 0,5 % der injizierten Aktivität direkt nach Injektion des Liganden. Danach erfolgt ein schnelles Auswaschen und nach etwa 17 min sind lediglich 0,1 % der injizierten Aktivität im Gehirn nachweisbar.

Ergebnisse: Die ¹⁸F-markierte Verbindung TC07 weist in Autoradiographien und Verdrängungsexperimenten einen sehr hohen Anteil an unspezifischer Bindung auf. Die durchgeführten Kleintierexperimente am μ PET zeigten, dass keine ausreichende Anreicherung des Radioligand [¹⁸F]TC07 im Gehirn erreicht wird. Ferner ist keine spezifische Bindung des Radioliganden an Regionen mit hoher GABA_A/ α_5 -Subtypverteilung nachzuweisen.

Als Ursache für die geringe Gehirnaufnahme wurde für TC07 die Eigenschaft diskutiert, als p-Gp-Substrat zu fungieren. In weiteren μ PET-Experimenten könnte zwar eine gewisse p-Gp-Affinität nachgewiesen werden, die jedoch nicht allein die geringe Hirnaufnahme erklärt. Weitere Faktoren wie der Effekte durch das Anästhetikum oder eine schnelle Metabolisierung des Liganden konnten ausgeschlossen werden. Welche anderen Faktoren noch eine Rolle spielen könnten (z.B. andere Effluxsysteme) bleibt unklar.

Basierend auf der hohen unspezifischen Bindung und der geringen Hirnanreicherung scheint TC07 kein geeigneter Ligand zur Visualisierung der GABA_A/ α_5 -Untereinheit darzustellen.

Danksagung

Diese Arbeit wurde finanziell unterstützt durch das Graduiertenkolleg 1044/1 „Entwicklungsabhängige und krankheitsinduzierte Modifikationen im Nervensystem“.

Synthese und nukleophile ^{18}F -Markierung von Tyrosin-Derivaten und aromatischen Modellverbindungen

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Einleitung: Die Parkinsonsche Erkrankung (PD) ist eine der meist verbreiteten neurodegenerativen Erkrankungen. Ursache für das Auftreten klinischer Symptome von Morbus Parkinson ist die Degeneration dopaminerger Neuronen in der Substantia nigra. Der am längsten eingesetzte Tracer für die Parkinson-Diagnostik ist 6- ^{18}F Fluor-L-dopa. Dieses wird zu 6- ^{18}F -L-Dopamin decarboxyliert und in dieser Form zusammen mit endogenem L-Dopamin in den intrasynaptischen Vesikeln gespeichert. Die präsynaptische Anreicherung liefert hierbei die klinisch relevante Information. Allerdings besitzt 6- ^{18}F Fluor-L-dopa keine idealen Tracereigenschaften zur Darstellung der Syntheserate des Dopamins, da durch zahlreiche Metaboliten ein sehr großer Aktivitätsuntergrund erzeugt wird [1]. Dagegen besitzt 6- ^{18}F Fluor-L-*m*-tyrosin gegenüber 6- ^{18}F Fluor-L-dopa einen deutlich vereinfachten Metabolismus. Sein Einsatz in der Routinediagnostik wird jedoch durch die schlechten radiochemischen Ausbeuten bei der elektrophilen ^{18}F -Fluorierung eingeschränkt [2].

Motivation: 6- ^{18}F Fluor-L-*m*-tyrosin ist ein Radiotracer mit großem Potential für die medizinische Diagnostik und die klinische Routine. Bei besserer Verfügbarkeit könnte es die wichtige Rolle des 6- ^{18}F Fluor-L-dopa übernehmen. Daher sollte eine Syntheseroute für einen geeigneten Markierungsvorläufer des 6- ^{18}F Fluor-L-*m*-tyrosins entwickelt werden, die eine möglichst effiziente nukleophile Markierung mit $^{18}\text{F}^-$ ermöglicht und die Anzahl der radioaktiven Reaktionsschritte gering hält.

Experimentelles: Die Darstellung der Markierungsvorläufer sollte durch eine mehrstufige Synthese, in deren Verlauf in *meta*-Position bromierte *p*-Dialkylaminoacetophenone mit enantiomerenreinen, aktivierten Aminosäurederivaten gekoppelt werden, erfolgen. Daher sollten an Amino- und Carboxylfunktion geschützte (*S*)-Aziridin-2-carboxylate und durch Metallierung in *meta*-Position aktivierte Aromaten synthetisiert werden. Nach der ^{18}F -Fluorierung sollte die Carbonyl-aktivierte Verbindung durch Baeyer-Villiger-Oxidation in *meta*-Position in den Acetylestere des geschützten 6- ^{18}F Fluor-L-*m*-tyrosin überführt und anschließend unter saurer Abspaltung der Schutzgruppen in das Produkt überführt werden. Als nukleofuge Abgangsgruppe wurde die Trialkylammonium-Gruppe gewählt, da sie bei nukleophilen ^{18}F -Fluorierungen die besten Ausbeuten erzielt und erst durch die Quarternisierung am Stickstoff aktiviert wird.

Ergebnisse: Der entscheidende Reaktionsschritt in diesem Synthesekonzept war die Darstellung eines enantiomerenreinen, für die nukleophile, Metallvermittelte Substitution an Aromaten aktivierten Synthons, ausgehend von Amino- und Carboxylgeschützten Derivaten des (*S*)-Serins. Trotz systematischer Variation der Reaktionsparameter wie

Lösungsmittel, Reaktionstemperatur, Reaktionsdauer und verwendetem Basenzusatz gelang es nicht, das für die Synthese des 6- ^{18}F Fluor-L-*m*-tyrosins zentrale Synthone darzustellen. Als Carbonyl-aktivierte, funktionalisierte Kopplungsreagenzien wurden drei verschiedene tertiäre Amine synthetisiert. Ihre Quarternisierung mit Methyltriflat gelang jedoch nicht. Die Markierung der Modellverbindung *p*-Nitroacetophenon führte unter Verwendung einer Labor-mikrowelle zu einer maximalen radiochemischen Ausbeute von 13 % bei 90 Sekunden Reaktionsdauer und einer Leistung von 90 Watt.

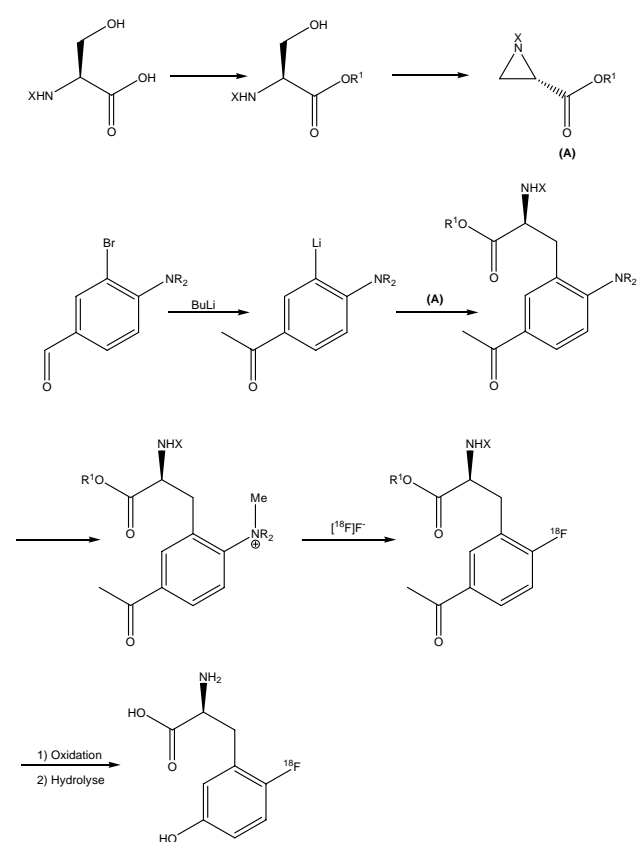


Abb. 1. Syntheschema des Markierungsvorläufers und nukleophile ^{18}F -Markierung

Ausblick: Basierend auf diesen Ergebnissen soll eine alternative Syntheseroute basierend auf einer klassischen Schöllkopf-Synthese untersucht werden. Das dabei entstehende Enantiomeregemisch müsste über HPLC an chiralem Säulenmaterial getrennt werden, da es sonst zu einer Racemisierung während der ^{18}F -Fluorierung kommen könnte [3].

Literatur:

- [1] DeJesus OT, Endres CJ, Shelton SE, Nickles RJ, Holden JE, J Nucl Med 38 (1997), 630
- [2] Nahmias C, Wahl L, Chirakal R, Firnau G, Garnett ES, Movement Disorders 10 (1995), 298,
- [3] Thierling T, Dissertation, Forschungszentrum Jülich 2002

Radioactive labeling of defined HPMA-based polymeric structures: Using [¹⁸F]FETos for *in vivo* imaging by Positron Emission Tomography (PET)

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Introduction:

Polymer-based therapeutics are of increasing interest in the development of nanomedical tools for the diagnosis and treatment of many diseases. For example, micelles have been studied for drug delivery applications. Thereby, the nonspecific interaction between proteins and polymer surfaces determines the *in vivo* fate of drug carriers. Particle-sizes, compositions, physical properties and surface chemistry influences the behaviour of nanomaterials *in vivo*. To understand and fine-tune these parameters for *in vivo* therapies or diagnostics, appropriate imaging strategies are needed. In this respect, non-invasive, quantitative, and repetitive whole body molecular imaging techniques such as Positron-Emission-Tomography (PET) would provide a significant advance in the understanding of the mentioned interactions.

Methods:

Defined statistic and block copolymers were synthesized by RAFT polymerization and labeled by [¹⁸F]FETos later on. The stability of the polymeric structures were determined 1 h and 2 h after the synthesis by SEC.

Results:

The polymeric structures are based on the biocompatible N-(2-hydroxypropyl) methacrylamide (HPMA). In order to achieve these structures, functional reactive ester polymers with a molecular weight within the range of 25000-110000 g/mol were aminolyzed by 2-hydroxypropylamin and tyramin (3%) to form ¹⁸F-labelable HPMA-polymer precursors. The fluoroalkylation procedure of the phenolic tyramin moieties by [¹⁸F]FETos provided radiochemical yields of ~ 80% for block copolymers and > 50% for statistic polymer architectures within a synthesis time of 10 minutes and at a reaction temperature of 120 °C. Total synthesis time including synthon synthesis, ¹⁸F-labeling and the final purification via size

exclusive chromatography took less than 90 minutes and yielded stable ¹⁸F-labeled HPMA-structures in isotonic buffer solution. Nodecomposition could be detected within 2 h.¹

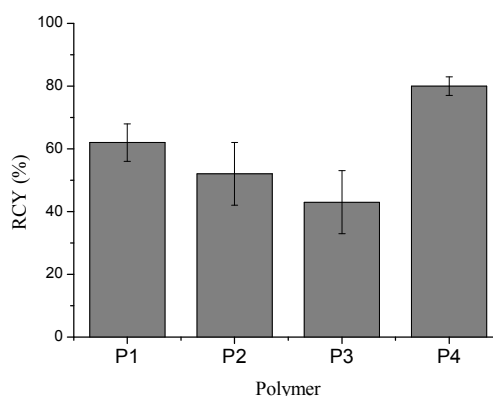


Figure 1: Corrected radioactive labeling yields (RCY) of the statistic copolymers **P1**, **P2**, **P3** and the block copolymer **P4** after 20 min at 100 °C using 3 mg of each precursor polymer

Conclusion:

A new versatile ¹⁸F-labeling strategy for polymeric particles has been introduced. Defined and functional HPMA based statistic and block copolymers have been synthesized by RAFT polymerization and labeled in high RCY of > 50% using [¹⁸F]FETos in a reaction time of ~ 10 min. Overall synthesis including [¹⁸F]FETos synthesis, polymer labeling and polymer purification via SEC was carried out in less than 90 min. The labeled polymer showed no decomposition.

References:

- ¹ Herth et al. (2009); Radioactive labeling of defined HPMA based polymeric structure: Using [¹⁸F]FETos for *in vivo* imaging by PET. Biomacromolecules (submitted)

NODAPA-OH and NODAPA-NCS: Mono- and multimeric six-coordinate Ga-chelators

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Introduction: The commercially available ⁶⁸Ge/⁶⁸Ga radionuclide generator systems and its recent improvement concerning on-line processing and labelling,¹ may provide a beneficial complement to nuclear imaging with established, cyclotron produced PET nuclides like ¹¹C and ¹⁸F. ⁶⁸Ga provides a high positron abundance of 89 % and an intermediate positron maximum energy. With its half-life (1.13 h) lying perfectly in between the half-lives of the most frequently used ¹¹C (0.33 h) and ¹⁸F (1.82 h), it provides excellent decay characteristics as a PET-radiolabel. On the other hand, the main group metal rapidly forms chelate-complexes with hard donor functions of four to six coordinating chelators. Adequate radioligand precursors meeting the coordination chemistry of gallium(III) with versatile conjugation possibilities are of high interest. The macrocyclic chelators DOTA and NOTA (Fig. 1) are established as frequently considered routes for the introduction of a ⁶⁸Ga-tag. Compared to open chain acyclic analogues, both provide complexes of superior kinetic and thermodynamic stability since gallium is irreversibly complexed at room temperature. DOTA remains the most frequently used chelator because of its better commercial availability and less challenging synthesis, although its six-coordinate nine-ring analogue NOTA displays higher stabilities and faster incorporation of Ga(III) at lower temperatures. Thus, we were interested in a time-saving and cost-effective access to a NOTA based versatile gallium chelator allowing convenient conjugation to various targeting molecules.

Experimental: Chelators 1-3 were synthesised from 4-substituted phenylacetic acids and TACN. To analyse whether the chain branch in one pendant arm affects the kinetic and thermodynamic characteristics of [⁶⁸Ga]NOTA-complex formation, labelling of NODAPA-OH, NODAPA-NCS, NODAPA-NCS₂ and NODAPA-NO₂ with generator produced and purified Gallium-68 was carried out in aqueous solution at pH = 2.8. Quality control was performed using an Agilent Zorbax C 8 column using 50 mM phosphate buffer and MeOH as eluent at 0.5 ml/min. The stability of the novel ⁶⁸Ga chelates was determined in a DTPA-challenge study at 25 °C and 37 °C employing 1 mM, 10 mM and 100 mM solutions of DTPA in water.

Plasma protein binding and transchelation to serum proteins *in vitro* was examined under physiological conditions in rat plasma. 4 MBq of [⁶⁸Ga]NODAPA-OH were incubated in 300 µL of

rat plasma from male adult Wistar rats, obtained via centrifugation of full blood. Samples of 50 µL were withdrawn after 1, 30, 60, 90 and 180 min and analysed by radio-TLC.

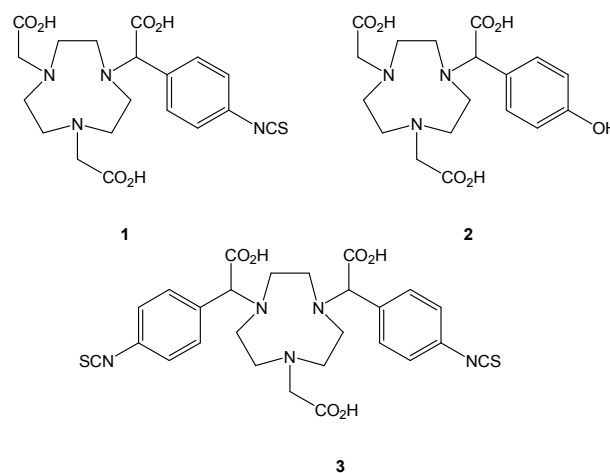


Figure 1. Novel NOTA-derived bifunctional chelators NODAPA-NCS (1), NODAPA-OH (2) and NODAPA-(NCS)₂ (3)

Results: Chelators 1-3 were obtained in 22 ± 6 % overall yield. Yields for ⁶⁸Ga(III) complex formation were very high (85±5 % already at 1 min) and comparable to those achieved for NOTA (Fig. 3).

The DTPA challenge experiment indicated >94% complex stability, in a similar range as the congener NOTA. In correlation to the DTPA-challenge, less than 2 % of non-[⁶⁸Ga]NODAPA-OH radioactivity was observed in rat plasma after 3 h.

Conclusion: Three novel NOTA-based bifunctional chelators have been obtained via a simple and efficient synthesis route. Compounds 1-3 provide excellent ⁶⁸Ga labeling and stability parameters. While offering -NCS and -OH functionalities, covalent coupling to various potential targeting vectors is possible.

References

[1] P. J. RiB, C. Kroll, V. Nagel, F. Roesch, *Bioorganic Medicinal Chemistry Letters* **2008**, *18*, 5364-7

Acknowledgement

This work was financially supported by DFG grant RO 985/23. The authors are grateful to the Fonds der Chemischen Industrie.

Synthesis and ^{68}Ga -radiolabelling of several N_3S_3 , N_3O_3 and NO_3 -type bifunctional chelators: Low-weight lipophilic Ga-chelates

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Introduction: In the present years, the positron-emitter ^{68}Ga undergoes a renaissance as generator-derived PET-nuclide for clinical routine. This is due to the recent improvements in generator performance of commercially available $^{68}\text{Ge}/^{68}\text{Ga}$ -generator systems, and post-processing of generator eluents. The latter includes purification of the ^{68}Ga by separation of metal contaminants as well as eluate concentration for labelling purpose.¹ Thereby a chemical generator system is transformed into a medical one. However, the application of $^{68}\text{Ga}(\text{III})$ for radiolabelling is somewhat limited to aqueous media and most reports on Ga-radiochemistry are concerned with polyamino-polycarboxylate chelators. The idea of lipophilic metal-chelates, dedicated for molecular imaging is not new. However, most of the earlier approaches did not specifically target bifunctional chelators, but elucidated the synthesis of rather lipophilic complex-precursors. This study reports ^{68}Ga -labelling and lipophilicity of mono- and bifunctional chelator-derivatives.

Experimental: The synthesis of a novel bifunctional N_3S_3 -type chelator, derived from 1,4,7-triazacyclononane, initial ^{68}Ga -radiolabelling and the determination of stability and lipophilicity of the compound are described. For comparison, the Ga-complex of tris-mercaptoethyl-1,4,7-triazacyclononane was also studied. Furthermore tetra- (NO_3) and hexadentate (N_3O_3) bifunctional chelators bearing phenol-donors were synthesised, labelled and their octanol/water partition coefficient was assessed experimentally.

Ga was eluted with different acetone-based, non-aqueous solvent systems providing n.c.a. $^{68}\text{Ga}(\text{acac})_3$ as labelling synthon. ^{68}Ga -labelling was performed in chloroform in a focused microwave synthesis system.

Results: The ^{68}Ga -labelled N_3S_3 chelate was obtained in a radiochemical yield of $80 \pm 5\%$ after a reaction time of 7 minutes. It remained intact over 3 h in a DTPA-challenge experiment, indicating sufficient stability for PET examinations. The 1-octanol/water partition coefficient $\log P$ was determined by HPLC, the results indicate rather lipophilic properties for the obtained chelate. The ^{68}Ga complexes of various mono and bifunctional chelators with lipophilic properties have been screened for their $\log P$ values. The results indicate, that these precursors indeed form stable lipophilic radiochelates. The bifunctional analogues of these complexes enable conjugation of targeting vectors for molecular imaging.

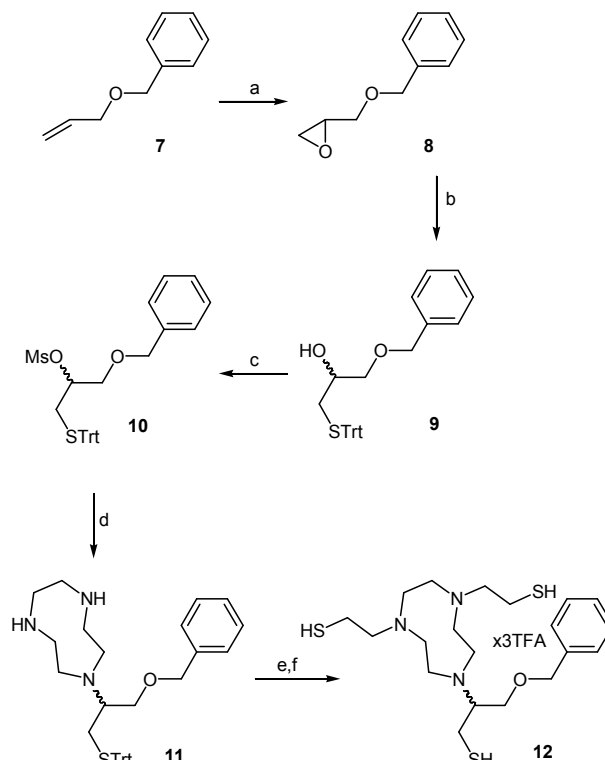


Figure 1: Synthesis of racemic model compound 12

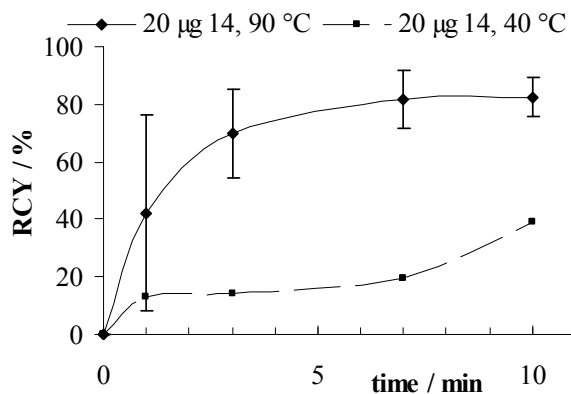


Figure 2. ^{68}Ga radiolabelling of precursor 12 at 40 °C and 90 °C.

References

- [1] D. A. Moore, P. E. Fanwick, M. J. Welch, *J. Inorg. Chem.* 1990, 29, 672 - 676;
- [2] A. E. Martell, R. J. Motekaitis, E. T. Clarke, R. Delgado, Y. Sun, *R. Ma, Supramol. Chem.* 1996, 6, 353 - 363;
- [3] U. Bossek, D. Hanke, K. Wieghardt, B. Nuber, *Polyhedron* 1993, 12, 1-5
- [4] R. Ma, M. J. Welch, J. Riebenspies, A. E. Martell, *Inorg. Chim. Act.* 1995, 236, 75 - 82

Acknowledgement

This work was financially supported by DFG grant RO 985/23. The authors are grateful to the Fond der Chemischen Industrie.

Synthesis and ^{68}Ga -radiolabelling of 2-desoxyglucose conjugated macrocyclic chelators.

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Introduction: [^{18}F]FDG is frequently used for the localization and staging of peripheral tumors and multiple other purposes. Although the approved imaging agent is readily available via reliable satellite distribution from local vendors, a generator based alternative would possess the potential to reduce overall cost and logistic effort. It might even increase the overall availability of the most frequently employed PET-examination, the FDG-scan.

This concept has already been examined,¹ e.g. for $^{99\text{m}}\text{Tc}$ -labelled ECD-desoxyglucose conjugates. Encouraged by the findings reported by those investigators, we were interested in a ^{68}Ga -labelled analogue for PET. ^{68}Ga provides a high positron abundance of 89 % and an intermediate positron maximum energy. With its half-life (1.13 h) lying perfectly in between the half-lives of the most frequently used ^{11}C (0.33 h) and ^{18}F (1.82 h), it provides excellent decay characteristics as a PET-radiolabel.

Experimental: Multiple mono- and divalent NOTA-desoxyglucose (NOTA-DG) and DOTA-desoxyglucose (DOTA-DG) were synthesised from 1,4,7-triazacyclonone and 1,4,7,10-tetraazacyclododecane in good yields. The compounds were labelled with prepurified n.c.a. [^{68}Ga]GaCl₃ in aqueous solution at pH = 2.8. Yields for ^{68}Ga (III) complex formation were in the usual range. The DTPA challenge experiment indicated high complex stability, in a similar range as the congener NOTA.

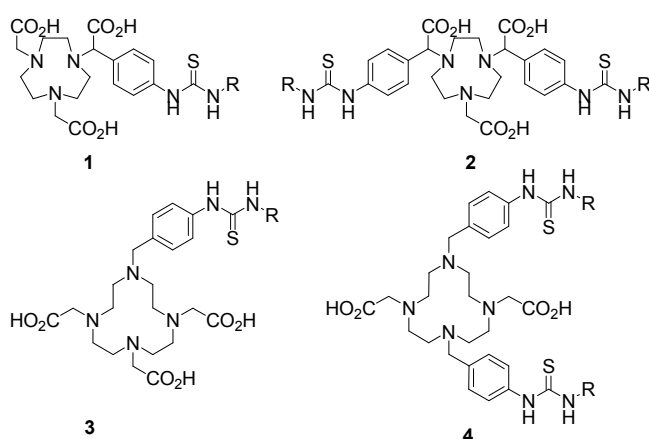
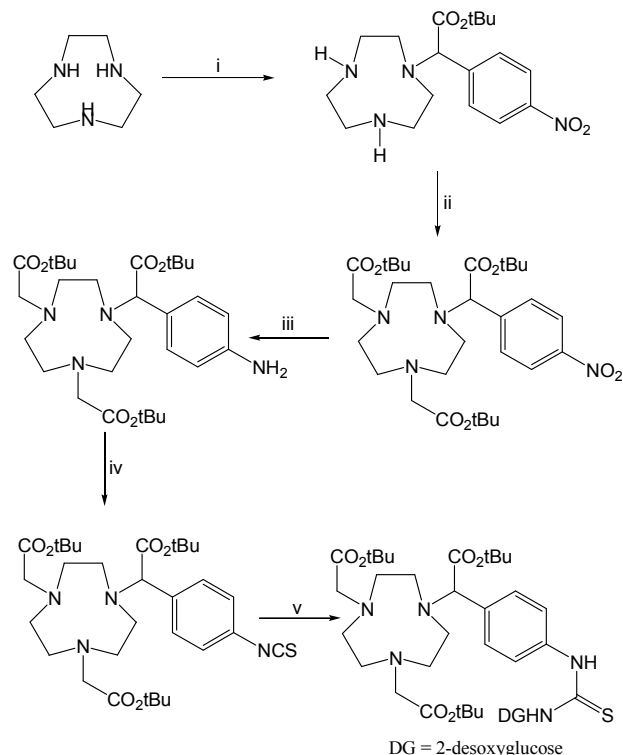


Figure 1. Structures of DG-conjugates



Scheme 1: Synthetic route to tris-tBu-NODAPA-NCS-NHDG¹. i) CH₂Cl₂, K₂CO₃, RT, 72 h, ii) MeCN, 75 °C, 14 h, iii) Fe, AcOH, 3h; iv) CCl₂S, CaCO₃, RT, 14 h.

Results: A series of novel macrocyclic chelator-desoxyglucose conjugates can now be examined for phosphorylation in a commercial glucose-hexokinase assay. If the novel compounds are still recognized by the GluT 1 as a substrate, further systematic imaging studies seem worthwhile.

References

[1] P. J. Riß, C. Kroll, V. Nagel, F. Roesch, *Bioorganic Medicinal Chemistry Letters* **2008**, *18*, 5364-7

Acknowledgement

The authors are grateful to the Fonds der chemischen Industrie

[⁶⁸Ga]HHDPD: A potential imaging agent for tumours and arteriosclerotic plaques

F. Zoller, P. Riss, F. Roesch

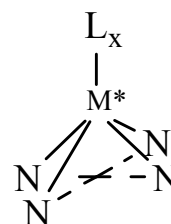
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Introduction: Generator-derived gallium-68 is highly relevant for molecular imaging strategies by means of position emission tomography (PET). The trivalent radiometal is used in a variety of current radiopharmaceutical developments. In this context, an effective post-processing of the generator-eluted gallium-68 plays a key role for following labelling procedures. This study reports a convenient method for ⁶⁸Ga-labelling of lipophilic porphyrin derivatives under anhydrous conditions using solid-phase derived gallium-68-acetylacetonate (⁶⁸Ga(acac)₃) in a microwave-enhanced radiosynthesis. Porphyrin derivatives accumulate in tumour tissue and atheromatous plaques and are established in photodynamic therapy (PDT).

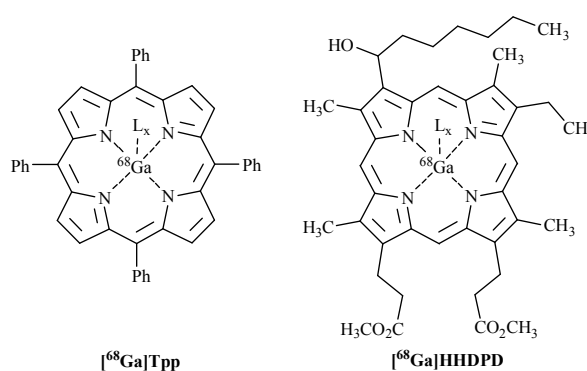
Experimental: ⁶⁸Ge/⁶⁸Ga-radionuclide generators utilizing TiO₂ to adsorb ⁶⁸Ge(IV) were used. The initial aqueous eluate was transferred online onto a cationic exchange resin to quantitatively absorb ⁶⁸Ga. From this resin, ⁶⁸Ga was eluted with different acetone-based, non-aqueous solvent systems providing n.c.a. ⁶⁸Ga(acac)₃ as labelling synthon. ⁶⁸Ga-labelling of porphyrin derivatives was performed in chloroform in a focused microwave synthesis system.

Results: More than 95% of the initially eluted ⁶⁸Ga was eluted from the cationic exchange resin with only 600 µl of a 98% acetone / 2% acetylacetonate mixture. Two different porphyrin derivatives, the simple symmetric meso-tetraphenyl-porphyrin and (3-(1-hydroxyheptyl)deuteroporphyrin dimethylester (HHDPD, FZ.MZ), were labelled in yields of >90% within 5 minutes using the ⁶⁸Ga(acac)₃ and diverse co-ligands in chloroform. Radiochemical purities of >95% were achieved by solid-phase extraction.

Conclusion: Two lipophilic porphyrin derivatives were rapidly labelled in high yields in a microwave-enhanced radiosynthesis. ⁶⁸Ga-labelling was achieved using solid-phase derived ⁶⁸Ga(acac)₃ as synthon under anhydrous conditions. Gallium complexation inside the macrocyclic tetrapyrrol-system was realised by diverse co-ligands. The novel ⁶⁸Ga-labelled porphyrin compounds are currently under investigation concerning their medical potential. Despite the synthesis of ⁶⁸Ga-porphyrin complexes, however, the procedure of online synthesis of ⁶⁸Ga(acac)₃ as a synthon for labelling reactions under non-aqueous conditions may be of general interest.



Scheme 1: Tetragonal pyramidal coordination of the five-coordinate metalloporphyrin (L_x: axial co-ligand, M*: trivalent metal ion)



Scheme 2: Structure of [⁶⁸Ga]Tpp and [⁶⁸Ga]HHDPD (L_x = phenol, gentisic acid).

References

- [1] Rösch, F., and Knapp, F. (2003) in *Handbook of Nuclear Chemistry* (Vertes, A., Nagy, S., Klenscar, Z., and Rösch, F., Eds.) pp 81-117, Kluwer Academic Publishers, Dordrecht
- [2] Zhernosekov, K. P., Filosofov, D. V., Baum, R. P., Aschoff, P., Bihl, H., Razbash, A. A., Jahn, M., Jennewein, M., and Rosch, F. *Journal of Nuclear Medicine* **2007**, *48*, 1741-8
- [3] Zoller, F., Riss, P., Montforts, F.-P., Roesch, F., *Bioconjugate Chemistry* **2008**, submitted

Acknowledgement

The authors are grateful to the Fonds der chemischen Industrie.

Syntheses and preliminary application of ^{68}Ga Schiff base derivatives for *in vivo* imaging of the p-Glycoprotein status in tumours

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Objectives

Cells of the human body contain very effective transport mechanisms to transport xenobiotics actively out of the cell. Thereby the intracellular concentration of drugs is lowered and a multidrug resistant phenotype results. The most important of these ABC-transporters is p-glycoprotein (pGP), which transports neutral and cationic structures under ATP-consumption. In many tumours pGP is over expressed leading to a very low concentration of several chemotherapeutics. In order to identify multidrug resistant tumours in advance, a PET-tracer would be helpful which should fulfil two features: (1) it should enter the cell easily (by passive diffusion) and (2) the tracer should be a substrate of the pGP and this transport should be inhibitable by pGP-inhibitors such as e.g. verapamil. Using the $^{68}\text{Ge}/^{68}\text{Ga}$ generator, novel ^{68}Ga -based Schiff base ligands provide interesting molecules accomplishing both requirements. Furthermore such radioactive tracers are applicable for cell studies as well as μ -PET imaging.

Methods

Based on a published ligand by Sharma et al. [1] six derivatives including the reference compound were synthesized in high yields, cf. Fig. 1. Labelling of these ligands was performed by usage of the $^{68}\text{Ge}/^{68}\text{Ga}$ generator which provides the positron emitter Gallium-68 ($T_{1/2} = 68$ min) in 400 μL of an acetone/HCl mixture [2]. ^{68}Ga labelling is performed in 400 μL 0.12 M Na-HEPES buffer by adding the ^{68}Ga fraction.

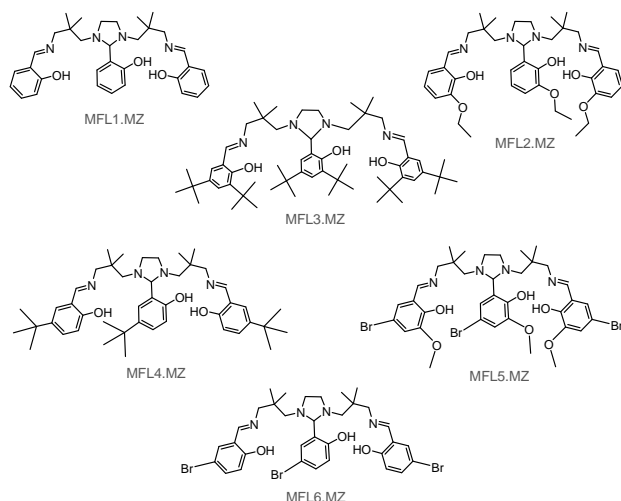


Fig. 1: ligands synthesized and investigated in this study

Through variation of reaction time, temperature and different amounts of the complex ligands, optimum reaction parameters for complex formation were tested. Analyses of radiochemical yield are carried out by TLC on silica and RP-18 phase. Cell studies on rat prostate carcinoma cells in presence or absence of verapamil

where performed for all ligands to prove that the ligands are transported by pGP. The most interesting ligand MFL6.MZ was used for first *in vivo* and *ex vivo* studies concerning uptake in solid growing rat tumours and compared to the published ligand.

Results

Labelling proceeds at temperatures between 25 and 75°C within 2 to 10 min in a total volume of 800 μL . Ligands are used in nanomole amounts only and the radiochemical yields are 50 to 95%. Cell essays showed that beside one ligand, which probably was trapped in the cell membrane, all others were transported by pGP. However, the uptake into the cell by non-ionic diffusion varied broadly between the ligands. The ligand MFL6.MZ was the most promising compound. Under normal conditions, 25% of the activity was taken up into the cell. When inhibiting the pGP-mediated efflux, this amount increased to 35%. Compared to the literature ligand (4.6 % respectively 8.2 % not inhibited and inhibited, respectively) this ^{68}Ga complex was selected for *in vivo* studies on a μ -PET.

Imaging ^{68}Ga -MFL6.MZ revealed a 3-fold higher accumulation in tumours compared to the reference tissue (testicles), whereas the literature compound [1] is only slightly enriched in the tumour.

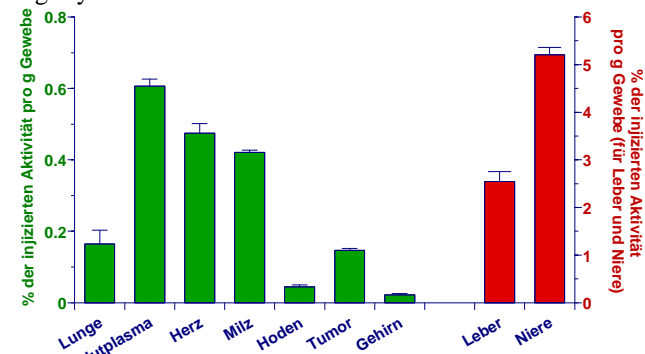


Fig. 2: biodistribution of ^{68}Ga -MFL6.MZ

Conclusions

Six Schiff base ligands were synthesized and labelled with ^{68}Ga in fast and high yielding complex formation. Tumour cell studies showed uptake in cells and transport processes of the complexes by pGP for six ligands. ^{68}Ga -MFL6.MZ was chosen for μ -PET imaging on tumour bearing rats demonstrating a high uptake in tumour compared to the literature compound. Further studies will involve blocking pGP *in vivo* and raising transport activity of pGP. With ^{68}Ga -MFL6.MZ it appears to be possible to identify patients with multidrug-resistant tumours pre-therapeutically in order to select adequate treatment regimes.

References

- [1] Sharma et al, J Nucl Med 46: 354-364
- [2] Zhernosekov et al, J Nucl Med 48: 1741-1748

Imaging of changes in p-Glycoprotein activity *in vivo* with ⁶⁸Ga-Schiff base derivatives

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Objectives

P-glycoprotein (pGP) is an active drug transporter of the ABC family pumping a wide number of xenobiotics out of the cell (under ATP consumption). Since many tumours overexpress this transporter and several chemotherapeutics are substrates of the pGP, the cytotoxicity of these drugs is markedly reduced leading to a multidrug resistant phenotype of tumours. Recent studies showed that the metabolic microenvironment of tumour affects the functional pGP-activity. Especially an extracellular acidosis (pH 6.6) leads to more than doubling of the transport rate resulting in a reduced cytotoxicity of chemotherapeutics *in vitro* and *in vivo* [1]. In this mechanism, MAP kinases (p38 and ERK1/2) play an important role in the signal pathway.

With Gallium-68 Schiff base complexes [2], in particular a novel derivative ⁶⁸Ga-MFL6.MZ, it became possible to visualize the functional activity of the pGP *in vivo* [3]. This compound allows the analysis of alterations of the tumour microenvironment (acidosis) as well as interrupting the signal pathway (inhibition of p38 and ERK1/2) on the pGP-transport activity non-invasively.

Methods

The ⁶⁸Ge/⁶⁸Ga generator provides the positron emitter Gallium-68 (T_{1/2} = 68 min) as a relatively inexpensive source of a PET nuclide. Using a recently published purification method [4] the ligand MFL6.MZ was labelled in a fast and easy process, directly ready for injection. Tumours were induced by subcutaneous injection of R3327-AT1 cells (which express pGP functionally) into the hind foot dorsum of male Copenhagen rats. Tumours were used when they had reached a volume of 1-2 mL. Acidification of the tumour was achieved by injection of small amounts (20 µL) of lactic acid (0.222 mM) directly into the tumour. The same amount of sodium lactate was injected into the contralateral tumour and served as control. The MAP kinases were inhibited by intratumoural injection of SB203580 (p38) and U0126 (ERK1/2).

Results

Acidifying the tumour led to a pronounced local reduction of the tracer accumulation in the tumour (Fig. 1-3). Since the tracer is a substrate of pGP, a reduced tissue concentration indicates a higher pGP transport activity. On average, the tracer concentration of acidified tumours was only 80% of controls.

In contrast, MAP kinase inhibitors lead to a reduced pGP transport rate which should result in a higher tracer accumulation in the tissue. Inhibition of p38 led to almost a doubling of the tracer activity as compared to the contralateral control tumour, whereas with the ERK1/2 inhibitor the concentration increased by 30%.

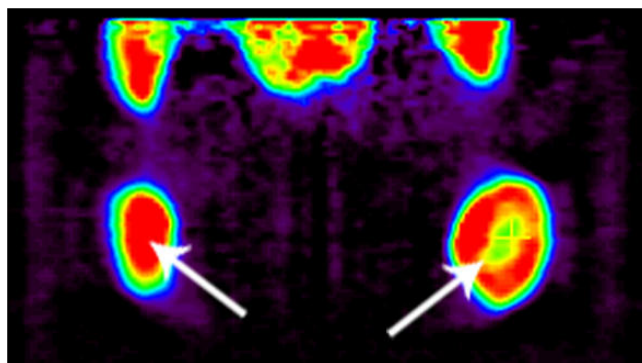


Fig. 1: coronal slice (acid injection in right tumour)

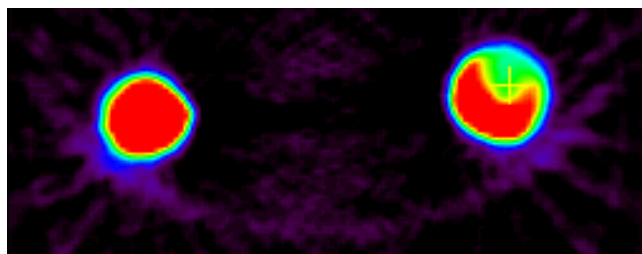


Fig. 2: transversal slice

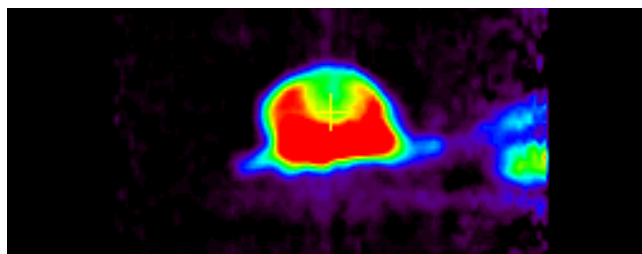


Fig. 3: sagittal slice

Conclusions

The newly developed Schiff base derivative MFL6.MZ labelled with the positron emitter ⁶⁸Ga allows a non-invasive monitoring of the functional pGP-activity in tumours. The results obtained with this new technique confirm previous *in vitro* studies that the transport rate in acidic tumour is markedly increased and that the MAP kinases p38 and ERK1/2 play a central role in the signalling pathway. The new tracer will be helpful in the development of new pGP-inhibitors in order to overcome multidrug resistance. In addition, this tracer will allow identifying patients overexpressing pGP, eventually needing a more aggressive treatment regime or other therapy modalities (e.g. radiotherapy).

References

- [1] Sauvart et al, Int J Cancer 123: 2532-2542
- [2] Sharma et al, J Nucl Med 46: 354-364
- [3] Fellner et al, in preparation
- [4] Zhernosekov et al, J Nucl Med 48: 1741-1748

Systematic labeling studies exemplified for a novel DO2A-tyrosine-derivative

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Introduction: The synthesis of radio-pharmaceuticals with high specific activities requires a time-efficient and high yield-labeling procedure [1], ideally avoiding final chromatographic separation. A lot of different parameters affect the ^{68}Ga -labeling yields of macrocyclic labeling precursors. On the example of a novel DO2A-amino acid derivative (DO2A-(butyl-L-tyrosine) $_2$) we performed systematic labeling studies in order to quantify the influence of reaction time, temperature of the reaction mixture and amount of precursor. Different pH-values were examined in presence and absence of buffer. Labeling yields of the pure labeling precursor were compared with those of its TFA-salt. Furthermore, a well working, time-effective solid phase extraction method was investigated to avoid a time-wasting HPLC-run to remove possible impurities. With all these optimization-steps the labeling yields and the specific activities of the products should be significantly increased.

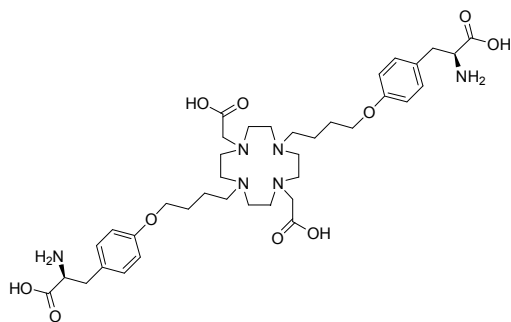


Figure 1: Structure of the labeling precursor DO2A-(butyl-L-tyrosine) $_2$

Experimental: The established $^{68}\text{Ge}/^{68}\text{Ga}$ -generator post-processing utilizing a cation-exchange resin was carried out prior to every labeling process [2]. The labeling experiments were carried out with the resulting ^{68}Ga fraction N2 in 5 ml labeling solution, like water or buffer, using different amounts of generator-eluate and labeling precursor at various temperatures. The mixture of labeling solution and precursor was preheated, then the ^{68}Ga was added. Different pH-values were reached, depending on the volume of generator eluate and the labeling solution. The starting pH-values were reaching from 8 to 10,5 utilizing aqueous sodiumhydroxid solution. A reaction under high pressure conditions was performed, too. The labeling mixture was heated to 175 °C for four minutes. The TFA-salts, as received from the HPLC, were removed from the labeling precursors using and ion-exchange resin.

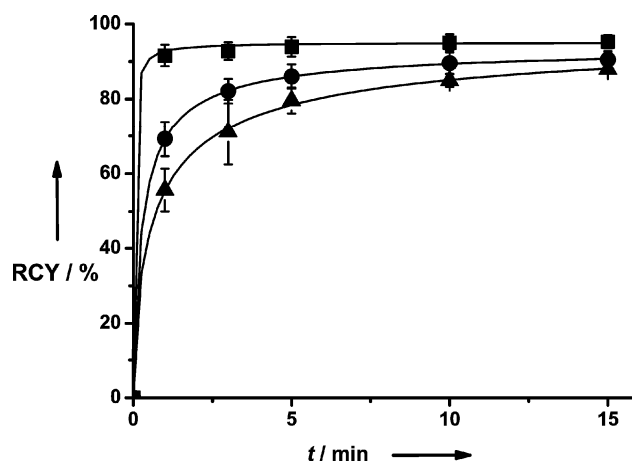


Figure 2: Radiochemical yields (RCY) of labeling of DO2A-(butyl-L-tyr) $_2$ with ^{68}Ga (50 ml generator eluate) at three different temperatures (90 °C (squares), 70 °C (circles), 50 °C (triangles)) in aqueous solution

The labeling yields of the desalted compounds were compared to the TFA-salts. Different solid-phase-extraction cartridges were tested for the purification of the product.

Results: Under the optimized conditions, with the desalted labelling precursor under the high pressure conditions, we achieved labeling yields of more than 99 %. Furthermore we established a solid-phase extraction method, to obtain, absolutely independent of the labeling yield, a radiochemical purity of more than 97 % ready to inject. The time for the total labeling and purification process including the ^{68}Ga -post-processing was reduced to only 13 minutes. The method showed a very high reproducibility and provides a low radiation dose. With all the optimizations we established a method to receive very high labeling yields in very short times. We achieved high specific activities up to 100 GBq/ μmol ready to inject in a multi injection vial after just 13 minutes. This method is well suited for the production of radiopharmaceuticals to be used in further evaluations, e.g. small animal PET-studies.

References:

- [1] I. Velikyan, G. J. Beyer, E. Bergstroem-Pettermann, P. Johansen, M. Bergstroem, B. Langstroem, Nucl Med Biol 35 (2008) 529
- [2] K. Zhernosekov, D. Filosofov, R.P. Baum, P. Aschoff, H. Bihl, A.A. Razbash, M. Jahn, M. Jennewein, F. Roesch. J Nucl Med. 48 (2007) 1741.

Acknowledgement:

This work was part of the COST-action D38.

Synthese von DO2A-Glibenclamid-Derivaten

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Einleitung: Diabetes mellitus ist eine Krankheit des Stoffwechselsystems an der 2006 allein in Deutschland 8 Millionen Menschen erkrankt waren. Die weltweite Anzahl an Erkrankungen belief sich auf 246 Millionen Menschen, was einem Anteil von etwa 6% der Weltbevölkerung entspricht. Die Tendenz ist weiterhin steigend, weshalb man mittlerweile auch schon von einer „Epidemie des 21. Jahrhunderts spricht“.

Man unterteilt für die praktische Therapie in absoluten (Diabetes mellitus 1) und relativem Insulinmangel (Diabetes mellitus 2). Form 1 ist eine Autoimmunerkrankung, die meist schon im kindlichen Alter auftritt und bei der die Insulinproduzierenden beta-Zellen der Bauchspeicheldrüse zerstört werden. Da sich der Diabetes erst manifestiert, wenn bereits 80% der Zellen zerstört sind, ist hier eine frühzeitige Diagnose erstrebenswert.

Sulfonylharnstoffderivate, zu denen auch Glibenclamid gehört, werden in der Therapie des Diabetes mellitus 2 eingesetzt. Sie binden an die SUR-Untereinheit der ATP-sensitiven K-Kanäle und steuern somit die Insulinausschüttung. Besonders auffällig sind die gute Bindungsaffinität von Glibenclamid ($K_i < 10$ nM) sowie die K_D -Werte, die zwischen 0,05 und 10 nM schwanken.

Dies alles macht Glibenclamid zu einem interessanten Target für die PET (Positronenemissionstomographie).

^{18}F -markierte Glibenclamid-Derivate führten jedoch zu einer zu hohen Aufnahme des Glibenclamids in die Leber im Vergleich zu der gewünschten Aufnahme in den Pankreas. Von daher ist es das Ziel weniger lipophile Glibenclamid-Derivate zu synthetisieren. Dies soll mit einer Kopplung an den makrozyklischen bifunktionellen Chelator DO2A gelingen.

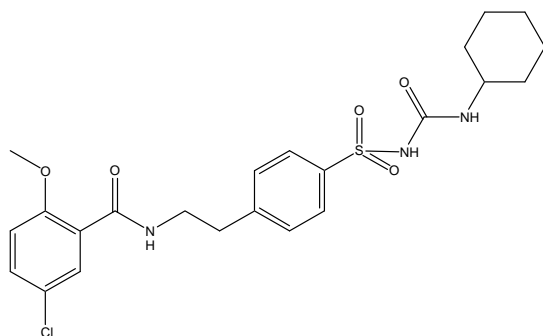


Abbildung 1: Glibenclamid

Experimentelles:

Die Synthese der kopplungsfähigen Glibenclamid-Derivate erfolgte ausgehend von 5-Brom/bzw. 5-Chlorhydroxybenzoesäure. Dabei wurde die Carboxyfunktion zunächst mittels Methanol geschützt und 1,3-Chorbrompropan als Linker angefügt. Anschließend wurde der Ester wieder gespalten und die Säure mit 4-(2-Aminoethyl)-benzulsulfonamid gekoppelt.

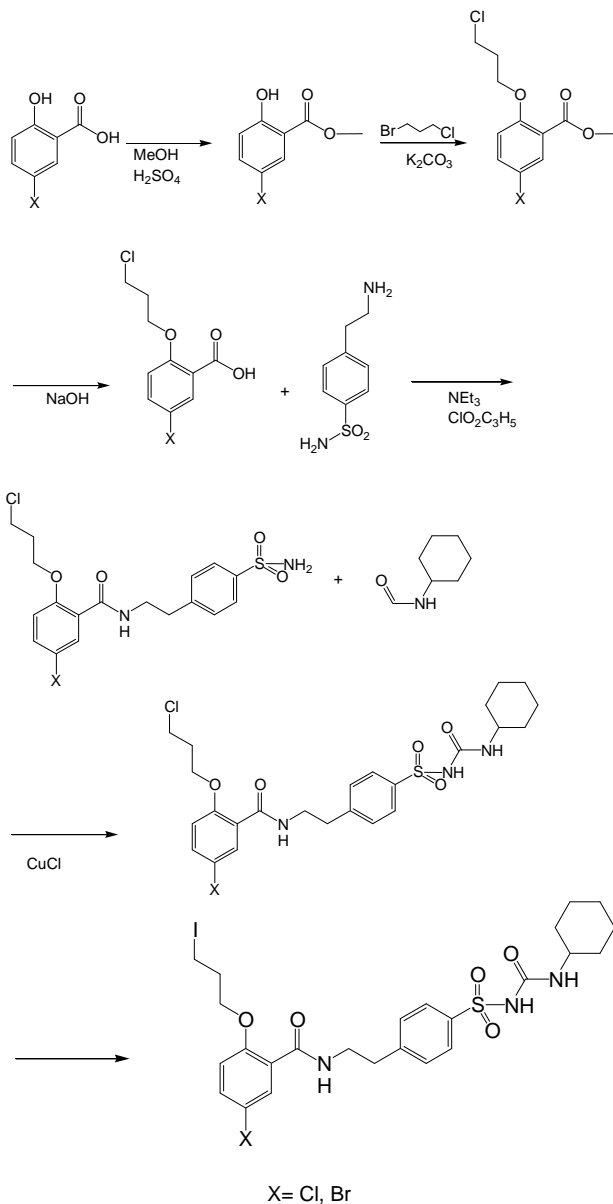


Abbildung 2: Reaktionsschema

Anschließend erfolgte die Kupfer (I)- katalysierte Umsetzung mit N-Cyclohexylformamid. Im abschließenden Syntheseschritt wurde das Chlor mittels Finkelsteinreaktion durch Iod ersetzt.

Ausblick: Die beiden synthetisierten Glibenclamid-Derivate sollen im nächsten Schritt an DO2A gekoppelt werden. Danach soll die Markierung des Komplexes mit ^{68}Ga erfolgen.

Literatur:

- [1] C.-Y. Shiue, A. Schmitz, R. Schirmmacher, G. G. Shiue, A. Alavi, *Curr. Med. Chem.– Immun., Endoc. & Metab. Agents*, 2004, 4, 271-280
- [2] R. Schirmmacher, Dissertation (2004)

Synthese von weiteren DO2A-Nateglinid-Derivaten zur Visualisierung der pankreatischen β -Zell-Masse

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Einleitung: Diabetes Mellitus Typ 1 ist eine weit verbreitete Stoffwechselerkrankung mit einer immunvermittelten Zerstörung der für die Insulinausschüttung verantwortlichen, pankreatischen β -Zellen der Langerhans'schen Inseln. Der Beginn der Krankheit ist oft bereits im frühen Kindesalter; klinische Symptome treten allerdings erst auf, wenn nur noch 10% der β -Zell-Masse vorhanden ist. Bisher gibt es keinen sensitiven Test, um das Fortschreiten der Krankheit zu bestimmen. Daher wäre es wünschenswert, diese Frühdiagnose mittels PET durchführen zu können [1]. Nateglinid ist ein Antidiabetikum der 3. Generation, das an transmembranständigen SUR1-Rezeptoren der β -Zellen bindet. Es wurde schon mit ^{18}F markiert, allerdings fand eine sehr hohe Aufnahme in der Leber statt und die β -Zell-Masse konnte nicht visualisiert werden. Ein ^{68}Ga -markierbares Nateglinid-Chelator-Derivat würde die Lipophilie der Verbindung deutlich senken und könnte einen geeigneten Kandidaten darstellen. Nach dem Versuch über eine zusätzlich eingeführte phenolische Hydroxygruppe an den Chelator zu koppeln [2], wurde nun die Carboxyl-Funktion verwendet.

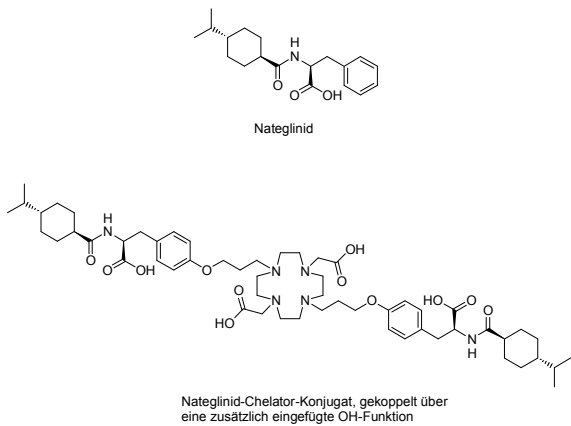


Figure 1. Strukturformeln von Nateglinid und dem über eine phenolische OH-Funktion an DO2A gekoppelten Derivat

Experimentelles: Die Synthese des Nateglinid-Derivats erfolgte analog zu der des Derivats mit phenolischer Hydroxygruppe, mit dem Unterschied, dass hier das Salz des D-Phenylalanins statt dem des D-Tyrosins verwendet wurde. Anschließend wurde mittels katalytischer Hydrierung die Schutzgruppe abgespalten und mit 3-Aminopropanol eine Amidbindung geknüpft. Die Hydroxygruppe wurde dann mittels Appel-Halogenierung in das kopplungsfähige Iod-Derivat überführt. Dieses soll nun mit DO2A gekoppelt, anschließend entschützt und mit ^{68}Ga markiert werden.

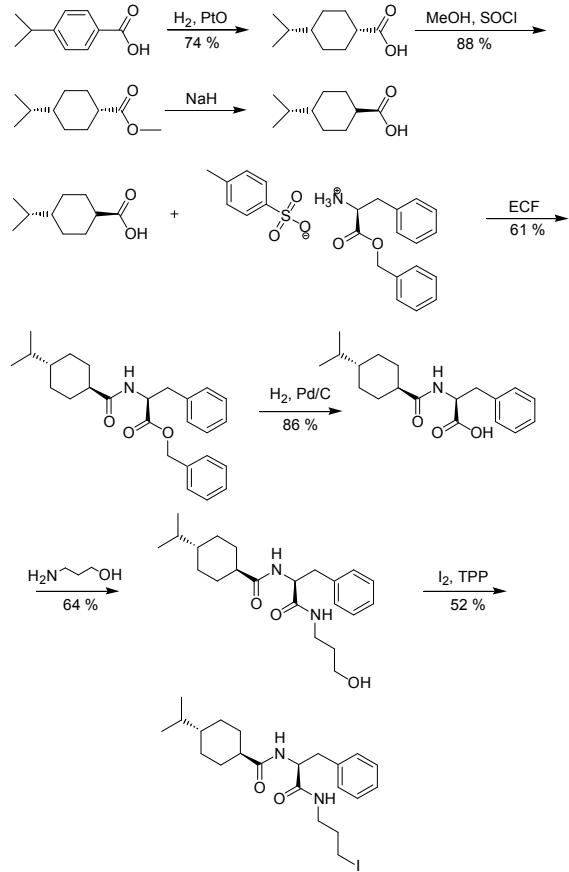


Figure 2. Syntheschema der kopplungsfähigen Nateglinid-Komponente

Ergebnisse: Die Synthese der kopplungsfähigen Nateglinid-Verbindung gelang in guten Ausbeuten über sieben Stufen. Diese soll nun mit DO2A zum Markierungsvorläufer gekoppelt und ^{68}Ga -markiert werden.

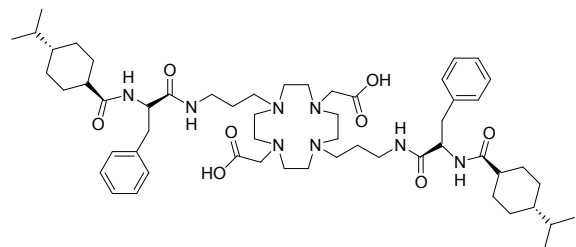


Figure 3. Strukturformel des über die Carboxylfunktion gekoppelten Nateglinid-DO2A-Markierungsvorläufers

Referenzen:

- [1] A. Pfützner, T. Forst, J. Beyer, The Microbiologist, 6, I, 1995
- [2] Jahresbericht 2007

Acknowledgement

Diese Arbeit ist ein Teil der COST-Action D38.

Phosphonate-complexes of Gallium-68 for bone tumour imaging

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Objectives

As ^{99m}Tc-phosphonates are well established tracers for the diagnoses of bone metastases using SPECT, analogue attempts for PET using the ⁶⁸Ge/⁶⁸Ga generator based ⁶⁸Ga tracers would be potentially useful. Therefore molecules containing phosphonate structure with binding affinities to apatite and being adequate complexing agents for trivalent Gallium could be considered as interesting vectors for the synthesis of generator-based PET-tracers for skeletal imaging. EDTMP, different triazacyclononane- (n=1-3 phosphonates) and DOTA-derivatives (tetraphosphonate) as well as new phosphonate structures were investigated.

Methods

Germanium-68 provides the positron emitter Gallium-68 as an easily available and inexpensive source of a PET nuclide. With the published concentration and purification method by Zhernosekov et al. [1] ⁶⁸Ga is obtained in 400 µL acetone/HCl mixture.

The first series of phosphonates (EDTMP, DOTP [2], NOTA-derivatives [3] and DO3A-ABn [4]) were labelled in 400 µL 0.12 M Na-HEPES buffer by adding the ⁶⁸Ga fraction. Through variation of reaction time, temperature, pH and different amounts of the ligands, optimum reaction parameters for complex formation were tested. Analyses of radiochemical yield were carried out by TLC on cellulose. Binding studies on synthetic apatite were applied to simulate the binding of the ⁶⁸Ga-phosphonates to bone structures. A second generation of bis-phosphonates (BPAMD, BPAPD and BPPED) was labelled, assayed concerning binding to apatite and investigated *in vivo* as well.

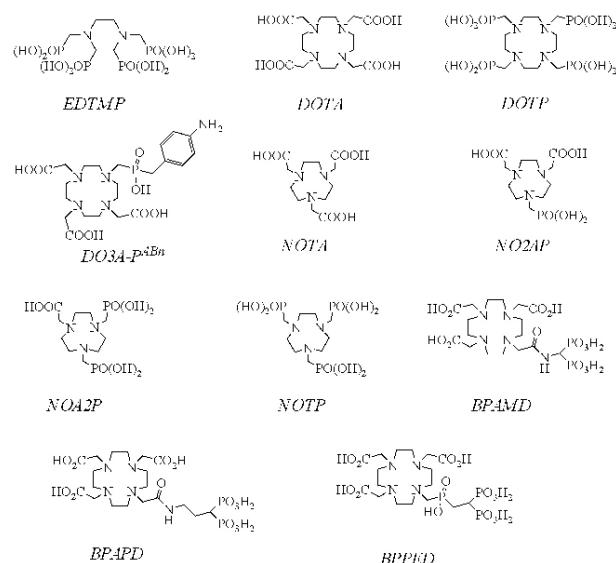


Fig. 1: ligands investigated in this study

Results

Labelling proceeds at temperatures between 25 and 75°C within 2 to 10 min in a total volume of 800 µL. Ligands are used in nanomole amounts only and the radiochemical yields are 50 to 95%. Strong and fast binding was observed for DOTP & EDTMP. Within the series of ⁶⁸Ga-triazacyclononanes with n=1-3 phosphonates, an increasing binding to apatite was observed.

The radiochemical yield of ⁶⁸Ga-DOTP was only 50%. *In vivo* experiments showed a relatively low stability of ⁶⁸Ga-EDTMP whereby large amounts of the ligand (>1.5 mg/kg body weight) has to be used. The bis-phosphonates showed also high binding to apatite and furthermore high stability *in vivo* in rats. Only nanomole amounts of these ligands are necessary for bone imaging.

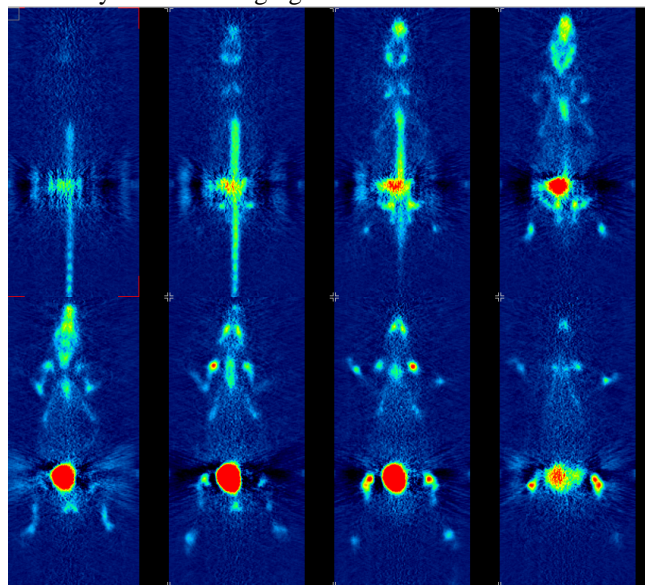


Fig. 2: coronal slices of a rat, 75-90 min after 15 MBq ⁶⁸Ga-BPAMD was injected

Conclusions

Syntheses of ⁶⁸Ga complexes are performed within 20 min after elution of the generator. Evaluations with synthetic apatite show high binding in a short time for ⁶⁸Ga-EDTMP and the ⁶⁸Ga-DOTP as well as the three new DOTA-derivatives BPAMD, BPAPD and BPPED. Preliminary µ-PET imaging on rats demonstrated bone uptake *in vivo* for ⁶⁸Ga-EDTMP and ⁶⁸Ga-DOTP. Due to the low stability of Ga-EDTMP and the low labelling yield of ⁶⁸Ga-DOTP the new ligands BPAMD, BPAPD and BPPED seem to be of more interest. µ-PET imaging of ⁶⁸Ga-BPAMD showed significant uptake in bone and high *in vivo* stability.

References

- [1] Zhernosekov et al, J Nucl Med 48: 1741-8
- [2] Sherry et al, Inorg Chem 35: 4604-12
- [3] Geraldes et al, Magn Reson Med 9: 94-104
- [4] Rudovsky et al, Org Biomol Chem 3: 112-7

⁶⁸Ga-Markierung von Makroaggregiertem Humanem Serum Albumin

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Einleitung: In der Lungenperfusionsszintigraphie werden die Durchblutungsverhältnisse der Lunge bildlich dargestellt. Zu diesem Zweck werden unter anderem mit ^{99m}Tc markierte HSA Mikrosphären (HSA = Human Serum Albumin) intravenös verabreicht. Die Partikel führen zu multiplen Mikroembolien in den durchbluteten Lungenabschnitten, sind aber wegen der geringen Stoffmenge für den Blutfluss nicht weiter von Bedeutung.

Die Aufnahmen erfolgen wiederum entweder als planare oder SPECT-Aufnahmen.

Ziel dieser Arbeit ist es nun kommerziell erhältliche Kits der Mikrosphären mit ⁶⁸Gallium zu markieren und damit für die PET nutzbar zu machen.

Methodik: Zur Komplexierung des ⁶⁸Ga werden die HSA Mikrosphären (HSA Mikrosphären B20 von ROTOP Pharmaka) mit einem Literatur bekannten Chelator (NODAPA-NCS) gekoppelt, entschützt und mit dem Generator-Eluat umgesetzt.

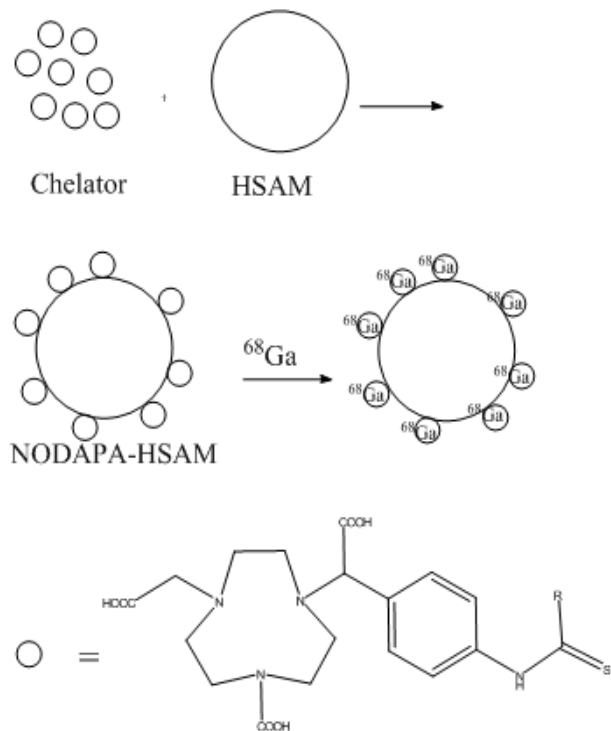


Abbildung 1: Kopplung und Markierung der Mikrosphären

Des Weiteren werden die Mikrosphären direkt, ohne vorherige Kopplung an einen Chelator, markiert. Dies hätte den Vorteil die Partikel analog zur Markierung mit ^{99m}Tc mit ⁶⁸Ga umsetzen zu können. Die direkte Markierung erfolgt zum einen direkt mit dem Eluat des Generators zum anderen nach der Methode von Green [1].



Abbildung 2: Markierung der Mikrosphären ohne Chelator

Der Chelator wurde nach Literatur [2] in einer mehrstufigen Synthese dargestellt.

Die Kopplung erfolgt analog zur Kopplung von DOTA an HSA Mikrosphären [3].

Zur Untersuchung der Stabilität der HSA Mikrosphären werden nach jedem Syntheseschritt Proben unter dem Mikroskop auf Veränderungen im Aussehen und der Fluoreszenzeigenschaften der Partikel vorgenommen.

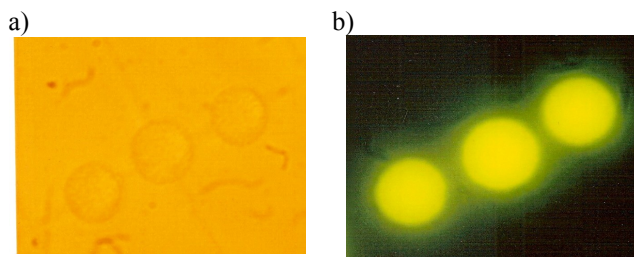


Abbildung 3: HSA Mikrosphären vor Behandlung
a) ohne Fluoreszenz
b) mit Fluoreszenz

Ausblick: Nach erfolgreicher Markierung der Mikrosphären mit ⁶⁸Gallium folgen in vitro und in vivo Untersuchungen.

Literatur:

- [1] Mathias C J, Green M A. A convenient route to [⁶⁸Ga]Ga-MAA for use as a particulate PET perfusion tracer. Appl. Radiat. Isotopes. 2008; 66: 1910-1912.
- [2] Kroll C, Diplomarbeit: Synthese makrozyklischer Liganden für Gallium(III), 2007, Universität Mainz
- [3] Schiller E, Bergmann R, Pietzsch J, Noll B, Sterger A, Johannsen B, Wunderlich G, Pietzsch H-J. Y-86 Labelled Human Serum Albumin Microspheres (DOTA-HSAM): In Vivo Stability Depends On Surface Structure Of The Spheres. Nucl. Med. Biol. 2008; 35: 227 - 232.

Danksagung:

Die HSA-Mikrosphären wurden dankenswerter Weise von Prof. Baum, Zentralklinik Bad Berka, zur Verfügung gestellt.

Synthesis of various benzamide-derivatives as potential targeting-vectors for D₂-Receptor imaging

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Institute of Nuclear Chemistry, Johannes-Gutenberg-University Mainz, Germany

Introduction:

Benzamides have been in the focus to target D₂-like receptors in the brain but also as imaging agents for tumors. Today, especially several (*S*)-(pyrrolidinyl)methyl-2-methoxy-benzamides such as [¹¹C]raclopride, [¹⁸F]fallypride, [¹²³I]IBMZ are used routinely for imaging D₂/D₃-receptor availability in the human brain and studying neurological disorders. In addition it was shown that these tracers may also be valuable for imaging tumors, which overexpress D₂-receptors. Concerning ¹¹C- and ¹⁸F-labelled derivatives, their routine application is limited due to the short half-life of the radionuclides and the need of a nearby cyclotron for producing the nuclides. Because of this PET nuclides such as ⁶⁸Ga which can be provided by a radionuclide generator are currently considered in novel tracers and may amend an enhancement in nuclear imaging. Thus, it was our intention to develop a reliable multi-gram synthesis of various (*S*)-N-[(1-allyl-2-pyrrolidinyl)methyl]-2,3-dimethoxy-5-propyl-benzamide derivatives bearing different functional groups at the 3-position of the propyl-group for allowing a direct and easy coupling with chelators necessary to coordinate radiometals.

Methods:

Because of different requirements for the various chelators it was the aim to consider different functional groups such as -NH₂, -N₃, -Br, -OH, -Tosyl, -COOH at the 3-position of the propyl group. Furthermore, a new synthetic route towards the tosyl derivative, i.e. the ¹⁸F-labelling precursor, was developed. Based on the published procedure [1] for the 3-hydroxypropyl derivative, the gently modified synthesis started from 2-hydroxy-3-methoxy benzoic acid to give the corresponding hydroxy-benzamide. Further reactions resulted in benzamides bearing various functional groups. The carboxy derivative was synthesised in a different and novel 8 step synthesis.

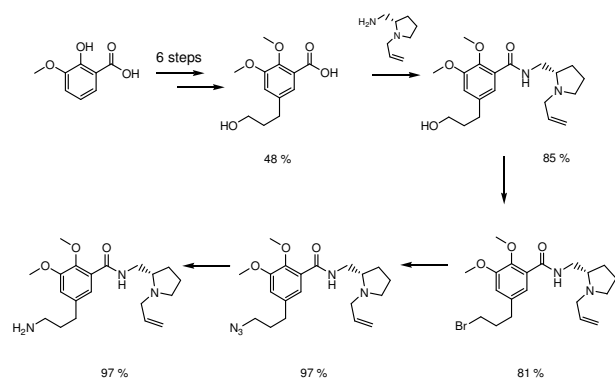


Figure 1. Synthesis of various benzamide derivatives

Results:

The desired hydroxy derivative was synthesised in excellent yields of 40% over 7 steps. Conversion of the hydroxyl group into the various groups was achieved via Appel-reaction, nucleophile substitution and Staudinger reduction. Replacement of pyridine by triethylamine increased the yield of the tosylation to over 85 %. The carboxy derivative was obtained from 3-methoxy-2-hydroxy benzoic acid over 8 steps.

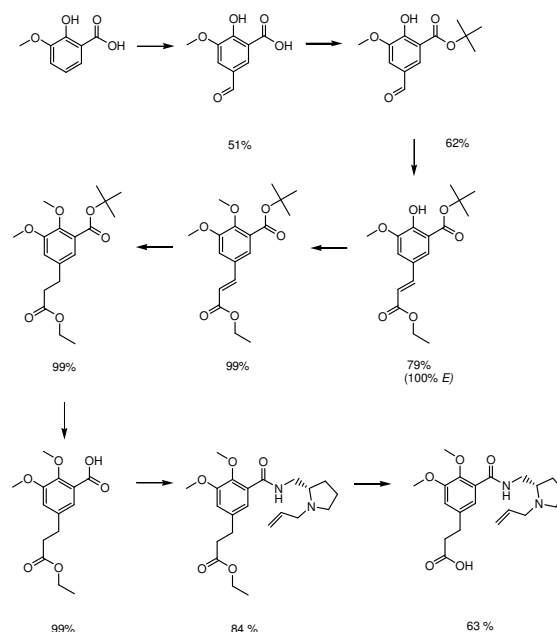


Figure 1. Synthesis of carboxy-fallypride

First reactions using the different derivatives gave N2S2-, and DOT₃A-conjugated benzamides.

Conclusions:

4 novel benzamide derivatives as potential targeting vectors were synthesised and are currently tested for their *in vitro* affinities. First conjugations to different chelators resulted in N2S2-, and DOT3A-benzamides. In additional experiments more conjugates shall be synthesised as well as radiolabelled.

The synthesis of the ¹⁸F-labelling precursor of [¹⁸F]fallypride was optimized for a multi-scale synthesis.

References

[1] Bishop J. E., Mathis C. A., Gerdes J. M., Whitney J. M., Eaton A. M., Mailman R. B., *J. Med. Chem.*, **34** (5), 1612-1624 (1991)

Synthesis and ^{99m}Tc -labelling of benzamide-derivatives for visualisation of D_2/D_3 -receptors

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Introduction:

Dopamine is the predominant catecholamine-neurotransmitter in the human brain, where it controls a variety of physiologic functions. Changes in the dopaminergic neurotransmission are linked to different neurological and psychic diseases, such as e.g. Parkinson's disease. Several tracers as [^{18}F]fallypride or [^{11}C]raclopride are used to image the D_2/D_3 -receptors *in vivo* by means of PET. Up to now, ^{99m}Tc -SPECT analogs that are highly selective for dopaminergic neurotransmitter receptor sites are uncommon. A ^{99m}Tc -labelled, at least medium-affine D_2 -postsynaptic receptor ligand would allow a cost-effective technique for the diagnosis of Parkinson disease.

It was our intention to synthesise ^{99m}Tc -containing fallypride derivatives introducing different chelators at the 5 position of the benzamide. Starting from fallypride as lead structure a number of derivatives were synthesised, which contained a chelator that is suitable for the labelling with ^{99m}Tc .

Methods:

Due to lacking information of structure activity relationships concerning modifications in position 5 of the benzamide, we first synthesised model compounds containing a phenyl ring connected to the 5 position of the Benzamide via an aliphatic chain. The phenyl ring can be considered as a comparable structure to the desired ^{99m}Tc -cp-(CO)₃ core. Variation of the alkyl chain length between the pharmacophore benzamide structure and the phenyl ring gave 12 compounds which were analysed towards their *in vitro* affinities. The *in vitro* affinities were determined for the following receptors D_1 , D_{2s} , D_{2l} , D_3 , D_4 , 5HT_{1A} , 5HT_{2A} and $\alpha 1$ using striatale parkin membranes and cloned chinese hamster ovar cells. After choosing the right chain length, 4 different chelators such as cyclopentadienyl, 2-pyridine-imine, amido-cyclopentadienyl and MAMA (N_2S_2) were linked to the benzamide structure. The corresponding rhenium complexes were synthesised, purified and determined towards their *in vitro* affinities. Finally, two compounds were labelled with ^{99m}Tc .

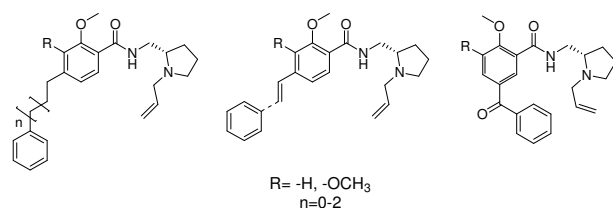


Figure 2. Structures of model benzamides – derivatives

Results:

The obtained phenyl-derivatives showed excellent affinities and selectivities towards the D_2/D_3 -receptors. The chain length of $n=3$ showed best values and was chosen for all further compounds. For the synthesis of the labelling precursors various novel benzamide-derivatives were synthesised. The introduction of the different chelators resulted in 4 labelling precursors and 3 rhenium-analogues.

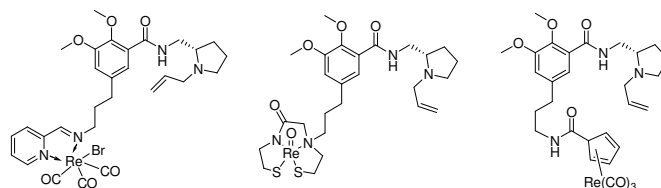


Figure 2. Structures of synthesised rhenium-analogues

Two rhenium-analogues showed good values for the D_2/D_3 -receptors of up to 70 nM and were labelled with ^{99m}Tc . Labelling with ^{99m}Tc was achieved using [$^{99m}\text{Tc}(\text{CO})_3(\text{H}_2\text{O})$]⁺ with labelling yields of up to 95%.

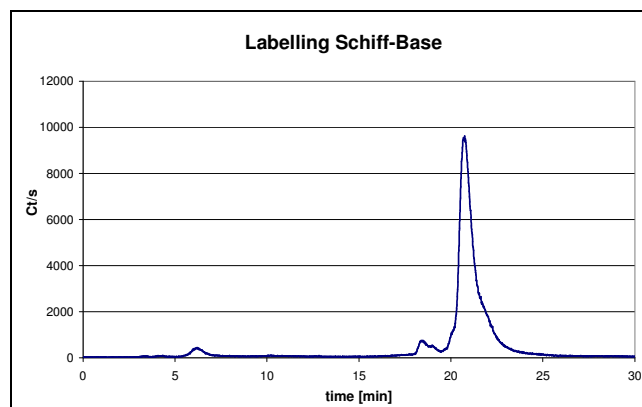


Figure 3 Labelling of the 2-pyridine-imine-derivative (HPLC profile)

Conclusions:

12 novel phenyl-benzamide model derivatives were synthesised retaining excellent affinities to D_2/D_3 -receptors. Four novel labelling precursors and 3 rhenium-analogues were prepared. Two of the rhenium-analogues showed good affinities and may have potential as ligands for the visualisation of the D_2/D_3 -receptors. In further experiments, their *in vitro* and *in vivo* behaviour shall be investigated.

Synthesis of [³H]Fallypride Using [³H]Methyl Nosylate

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Introduction:

Dopamine is the predominant catecholamine-neurotransmitter in the human brain. Malfunctions in the dopaminergic neurotransmission are associated to several neuropsychiatric diseases, such as Parkinson's, Alzheimer's and Huntington's disease as well as schizophrenia. Various radiolabelled benzamides which are highly selective towards the D₂/D₃-receptors have been developed and are used to visualise these receptors *in vivo* via PET/SPECT. One of the most promising structures is the ¹⁸F-labelled benzamide [¹⁸F]fallypride. Due to its excellent affinities and selectivity it is an ideal tracer for visualizing receptor availabilities in brain regions with high and low receptor density. However, long-term experiments as e.g. autoradiographies and replacement studies are limited to the short half-life of [¹⁸F]fluorine. The introduction of tritium into a molecule, with its half-life of 12.3 a and a maximum β-energy of 18.6 keV, provides a way to accomplish the desired experiments, also providing higher precision in autoradiography. Consequently, it was the aim to introduce a tritium label into the original fallypride structure.

Methods:

Tritium can be introduced via many different routes into organic molecules. One of the most favoured synthetic pathways is the halogen/tritium-exchange using tritium gas and catalysts like palladium. Due to the allyl-group and the obliged reduction of the double bond this pathway cannot be implemented. Another possibility of introducing the desired tritium label is the methylation via a tritium methylating agent such as [³H]methyl iodide. The 2-methoxy group in the benzamide structure offers a good approach for the introduction of the tritiated methyl-group.

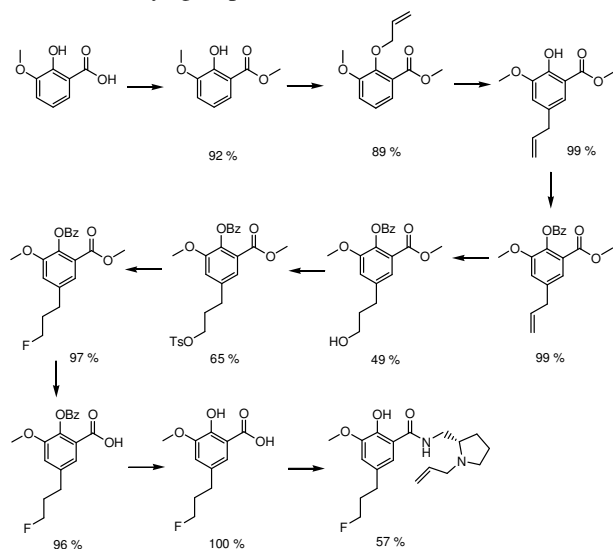


Figure 1. Synthesis of norfallypride

Based on the published procedure [1] for [¹¹C]fallypride, the 2-hydroxy-precursor was synthesized with slight modifications. After optimisation of the labelling reaction using ¹H-analogues of the tritium methylating agents, the final tritium labelling of 3.5 mg desmethyl-precursor with 40 mCi [³H]methyl nosylate was carried out by RC Tritec AG (Teufen, Switzerland).

Results:

The desired labelling precursor was synthesised starting from 2-hydroxy-3-methoxy-benzoic acid using a benzyl-protecting group in 10 steps with an over all yield of 14%. First labelling for optimisation of the labelling with methyl iodide resulted in yields below 50% (determined via HPLC). The use of methyl nosylate, Cs₂CO₃ and DMF at room temperature resulted in 98% yield. These conditions were chosen for the [³H]-labelling. The [³H]methyl nosylate was synthesized starting from tritium gas over 5 steps, purification via semi-preparative HPLC resulted in 15 mCi of [³H]fallypride with a radiochemical purity of >99 % (HPLC). Starting from [³H]methyl nosylate the radiochemical yield was 38%.

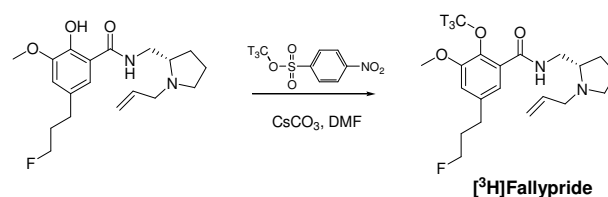


Figure 2. Labelling with [³H]methyl nosylate

Conclusions:

A multi-step synthesis starting from 2-hydroxy-3-methoxy-benzoic acid provided the 2-hydroxy-labelling precursor. After optimisation of the labelling reaction, the precursor was reacted with [³H]methyl nosylate to give [³H]fallypride. HPLC purification afforded 15 mCi [³H]fallypride with a radiochemical purity of >99 % (HPLC).

Further experiments will focus on *in vitro* and *ex vivo* autoradiographic tests analysing local high-resolution D₂-like receptor distributions and densities

References

[1] Mukherjee J., Shi B., Christian B.T.; Chattopadhyay S., Narayanan T.K., *Bioorganic and Medicinal Chemistry*, Volume 12 (1), 2004, pp. 95-102

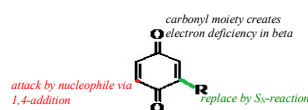
[¹⁸F]-Labeled quinones as imaging tools for proteins

D.E. Borchmann², E.J. Millings³, J.M. Hooker¹, J.S. Fowler¹

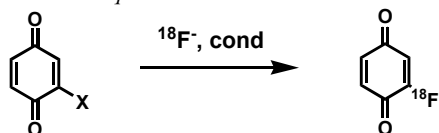
¹Brookhaven National Laboratory, NY, USA, ²Johannes Gutenberg-Universität, Mainz, Germany, ³Suffolk County Community College, NY, USA

Introduction

Tracking protein location and gaining insight into protein function is crucial for better understanding of diseases and metabolism. Imaging agents, however, should not significantly change the protein's three-dimensional structure and its function. Hence our aim was to develop a small (commercially available) precursor molecule to be labeled with fluorine-18 which can easily be attached to a protein's side group (lysine or cysteine). Substituted quinones can be labeled by substitution reactions and attached to proteins via Michael addition.



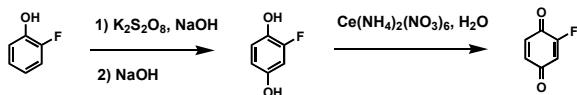
Scheme 1: quinone characteristics



Scheme 2: substitution reaction

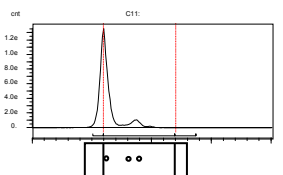
Results and discussion

As a start-up, “cold” 2-fluoro-1,4-benzoquinone was synthesized in a two-step synthesis (by Elizabeth Millings, fellow student) from *o*-fluorophenol via the 2-fluoro-1,4-hydroquinone (see scheme 1). This molecule served as a standard for TLC and HPLC in the “hot” reactions and as a tool to simulate the peptide or protein interactions with molecules like *N*-acetyl-cysteamine. These reactions were always successful, although isolation of the product still seems to be challenging.



Scheme 3: synthesis of 2-fluoro-1,4-benzoquinone

In the “hot” reaction, commercially available quinones were screened, like 2-chloro-1,4-benzoquinone (CBQ), 2,5-dichloro-1,4-benzoquinone (DCBQ) or 2,3,5,6-tetrachloro-1,4-benzoquinone (TCBQ). Especially TCBQ showed promising results, though it is not a good precursor (α,β -unsaturated carbonyl system already “blocked” by the four chloro substituents) and results were not reproducible.

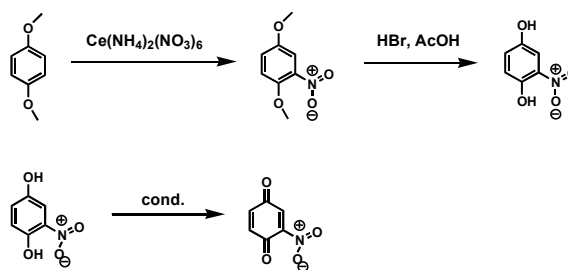


Scheme 4: typical radio-TLC of S_N-reaction

In the following, quinones with better leaving groups were synthesized, such as 2-bromo-1,4-benzoquinone (BBQ), 2-iodo-1,4-benzoquinone (IBQ) and 2-nitro-1,4-benzoquinone (NBQ).

BBQ and IBQ could not provide significantly better radiochemical yields. The reaction with IBQ did not even lead to the desired product.

NBQ could not be tested “hot”, because the precursor synthesis always failed in the oxidation step from hydroquinone to quinone. We assume that NBQ is too strong an oxidizing agent and thus has to be used in a one-pot reaction, if at all, which leads to the problem of purification.



Scheme 5: synthetic route to 2-nitro-1,4-benzoquinone

Conclusions

[¹⁸F]-2-fluoro-1,4-benzoquinone was synthesized successfully, which is an enhancement to older radioactive labeling agents in so far that only one step is necessary and that the precursor is commercially available.

Yields still have to be improved or a better precursor molecule has to be found.

References

- [1] Cai, W., Zhang, X., Wu, Y., Chen, X.; *J. Nuclear Medicine* 2006, 47 (7), 1172-1180
- [2] Knalves, *J. Am. Chem. Soc.* 1934, 56, 670
- [3] Mason, D.E., Liebler, D.C.; *Chem. Res. Tox.* 2000, 13 (10), 976-982
- [4] Carlson, B.W., Miller, L.L.; *J. Am. Chem. Soc.* 1985, 107 (2), 479-485

Acknowledgements

Thanks go to my mentor Dr. J. Hooker, to my fellow student E.J. Millings, who introduced me to the project and to [¹⁸F]-labeling basics, to Dr. J. Fowler and the imaging group and to Prof. Dr. F. Rösch and the DAAD.

Synthesis of the selective estrogen receptor modulator STX and of a precursor for the radio labelling of STX with radioactive methyl iodide

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Introduction

In the brain, rapid estrogen responses through non genomic pathways have been found. Those responses are not caused by estrogen receptor mediated gene transcription. Recently, a molecule was reported, which does not bind to nuclear estrogen receptors (ER) but showed estrogen like effects. This non-genomic response is induced by rapidly inhibiting G-Protein-coupled inwardly rectifying potassium channels (GIRK) activation in hypothalamic γ -amino butyric acid and proopio-melanocortin neurons.

This estrogen-like effect suggests that a novel estrogen receptor exists, which is different from nuclear ER. To image the distribution and concentration of these receptors in the brain, the compound STX had to be synthesized and labelled with [¹¹C-methyl iodide].

Experimental

Our synthesis of a reference compound (STX itself) and a labeling precursor lacking a methyl group were guided by the original literature report. However, during the course of the synthesis we examined several of the transformations in detail and in many cases optimized the literature procedure to increase yield and/or to improve the scalability of the synthesis.

The first step in the synthesis of STX was a titanocene-mediated alkylation of an alkyne that was quenched with bromine to selectively yield the E-Olefin (A). The isolated bromoalkene was then used in a Negishi-type reaction for the tetrakis-(triphenyl-phosphine)-Pd (0) catalyzed cross coupling of the organozinc intermediate with the tertbutoxybromo-benzene to give the phenyl-4-tert-butoxy-phenyl-trimethylsilylbutene (B). The trimethylsilyl-group was replaced through treatment of (B) with a bromine solution in anhydrous dichloromethane to yield the vinyl bromide (C).

At this stage of the synthesis two inseparable stereoisomers were formed in the ratio 2:1 favouring the Z isomer. The mixture of the two stereo isomers was then transmetalated with BuLi and a dry stream of carbon dioxide was conveyed through the reaction mixture to yield the carboxylic acids (D).

In a nucleophilic substitution of the 2-(dimethylamino) ethyl chloride by the Boc-protected 4-aminophenol and subsequent removal of the protecting group the para substituted Aniline (E) was obtained. The E/Z mixture of the enoic acid was then coupled with HBTU and DMAP to the para-substituted aniline (E) to obtain a mixture of amides. Hydrolyses of the 4-terbutylether resulted in the compounds ST-X and ST-Y. Direct N-demethylation of ST-X failed so the precursor synthesis starts from compound E to yield the monomethylated version of the ST-X, that can be labelled with ¹¹C-methyl iodide. (Figure 2).

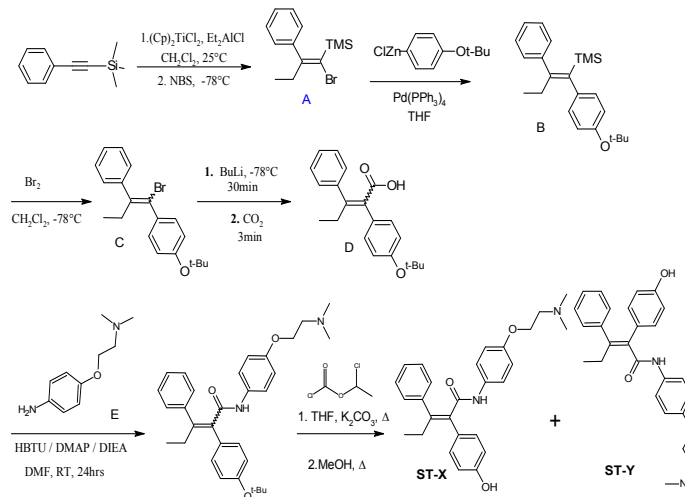


Figure 1. Synthesis of the reference compound ST-X

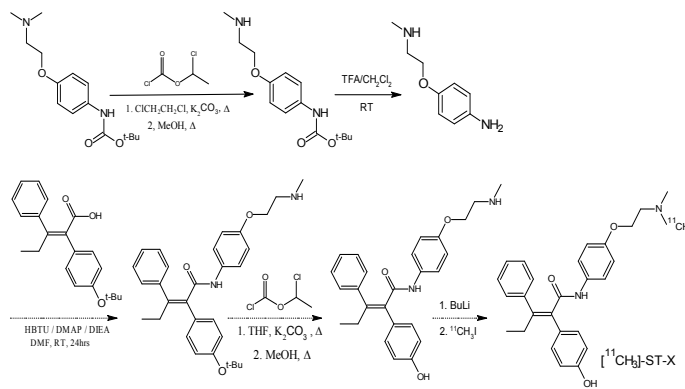


Figure 2. Precursor synthesis and radio labelling with [¹¹C₃-I].

Results: The desired molecule ST-X could be successfully synthesized but not separated from co-forming stereoisomer ST-Y. At the time of writing no ¹¹C-labelled ST-X had yet been obtained.

References

- [1] Sandra C. Tobias, Jian Qiu, Martin J. Kelly, Thomas S. Scanlan. *ChemMedChem* 2006; 1: 565-571.
- [2] Ross V. Weatherman, Nicola J. Clegg, Thomas C. Scanlan. *Chemistry and Biology* 8 (2001) 427-436

Acknowledgment:

I want to thank Prof. Dr. Joanna Fowler, the BNL, Chemistry Department, and Prof. Dr. Rösch. Funding by *Studienstiftung des deutschen Volkes* and DOE.

Progress towards labeling modafinil with [¹¹C]Cyanide

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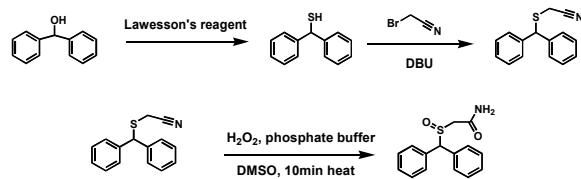
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Introduction

Modafinil is a wake-promoting drug for the treatment of narcolepsy, a common disease in shift workers. Narcolepsy manifests itself in excessive day-time sleepiness, cataplexy (muscular weakness) and abnormal rapid eye movement during sleep phases^[1]. The drug modafinil alleviates the indications and is FDA approved since 1998. The exact mechanism of action, however, is still unknown and should be explored by labeling modafinil with [¹¹C]-cyanide and consequently using it in PET (positron emission tomography) studies.

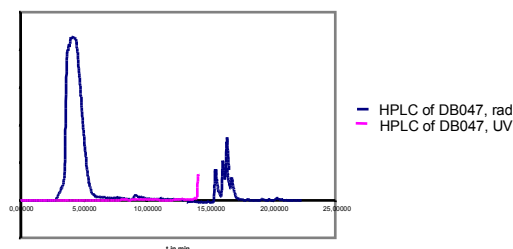
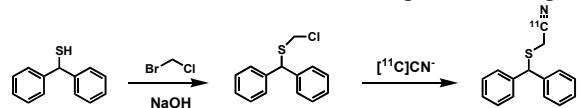
Results and discussions

As a standard for TLC and HPLC we first synthesized non-radioactive modafinil in a three-step synthesis from Benzhydrol. This is a new and shorter synthetic route to modafinil and has not been reported before.



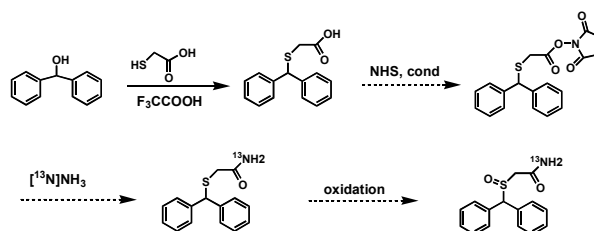
Scheme 1: synthesis of a modafinil standard

Originally, modafinil should be labeled with the positron-emitter carbon-11 due to its convenient half-life (21min) and the fact that the insertion of this isotope would not change the molecule in its stereochemistry. (Benzhydrylsulfanyl)methyl chloride was synthesized as a precursor for the “hot” reaction and the chloride was exchanged by [¹¹C]-cyanide in the following. While screening reactions by HPLC “cold”, though, we often observed the formation of a side product with a retention time of 10.9min, which we could not further identify. This byproduct, together with others, also occurred in the “hot” reaction and thus made purification and characterization of the desired product tough.



Scheme 2: “hot” reaction, first step, and radio-HPLC

Although the oxidation reaction to modafinil had been performed “cold” with promising yields, it could not be attempted “hot” due to the above mentioned problems. A new approach now is to synthesize a reactive carbonyl precursor molecule which is then labeled with [¹³N]-ammonia.



Scheme 3: new synthetic route to modafinil

Conclusions

A new synthesis for “cold” modafinil has been successfully developed. Efforts to synthesize [¹¹C]modafinil by using [¹¹C]KCN and (Benzhydrylsulfanyl)methyl chloride as starting material, however, did not lead to the desired product [¹¹C]-(Benzhydrylsulfanyl)methyl cyanide, which would have been then oxidized to modafinil. For this reason, current research focuses on labeling with nitrogen-13 as described above.

References

- [1] Billiard, M. *Neuropsychiatric Disease and Treatment* 2008, 4 (3), 557-566
- [2] Prisinzano, T.; Podobinski, J.; Tidgewell, K.; Luo, M.; Swenson, D.; *Tetrahedron Asymmetry* 2004, 15, 1053-1058

Acknowledgements

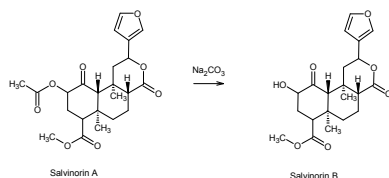
I would like to thank Dr. Jacob M. Hooker for being a great mentor and teaching me many new skills and perseverance. Also, I want to thank the imaging group at BNL, especially Dr. Joanna S. Fowler, for making my stay possible and integrating me into the group. I also thank Prof. Dr. F. Rösch for motivating me to apply for this project and for supporting me. Finally, thanks go to DAAD for funding.

Brain studies with Salvinorin A, Salvinorin B and exploration of ways to synthesize a starting material for using EOM-Salvinorin B as another tracer for brain imaging.

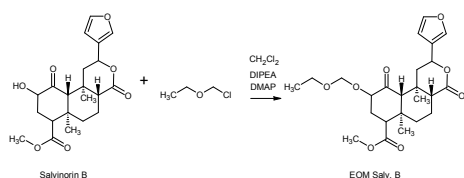
M. Best¹, J. Hooker², C. Shea², M. Schueller², Y. Xu², P. Carter², J. Fowler²

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Introduction: Salvinorin A is a hallucinogenic drug extracted from *Salvia divinorum*. As a selective agonist of the κ -opioid receptor it has a very strong, but short effect. It causes visual hallucinations and behavioural impairment within seconds when smoked. This drug is a very interesting tool for medical research. There is not only a very big therapeutic potential, but also the chance of understanding the functioning of receptors. Using this knowledge for analgesia and neuroprotection are only examples for the opportunities of this research. After extraction of Salvinorin A we synthesized the important derivate Salvinorin B, which can be obtained by deacetylation of Salvinorin A:



It is already known that this derivate shows a dramatically lower affinity and potency as the Salvinorin A by itself. This may suggest that the acetate is involved in separate, synergistic interactions with the receptor. One of our interests was the synthesis of EOM-Salvinorin B (EOM: ethoxymethyl ether) which is known to be a very potent and selective agonist of the κ -opioid-receptor. This suggests that there must be an additional interaction between the terminal alkyl group and the receptor which is leading to the much higher affinity:



Experimental: Salvinorin A and B were obtained like described before [1]. For the synthesis of EOM [2] 0.2 grams (0.5 mmol) of Salvinorin B were dissolved in dichloromethane. 2.0 equivalents of EOM-Cl were added dropwise. 2.1 equivalents of DIPEA (base) and 0.25 equivalents of DMAP (catalyst) were used. The mixture was stirred for 15 hours at room temperature. Approximately 25 mL CH_2Cl_2 were added to the mixture with a white precipitate. This solution was washed twice with 1M HCl and once with a saturated aqueous solution of NaCl. The organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. Yield: 83.4 %, a light yellow substance. A very small amount of the light yellow substance was dissolved in dichloromethane for the TLC analysis. Using the ratio 1:1 hexanes and ethyl acetate led to an R_f - value of 0.6 for the EOM-Salvinorin B and 0.3 for the Salvinorin B. For the method of ^{11}C labelling the demethylation in position C18 was necessary. The synthesis of the necessary acid compounds and the method of ^{11}C labelling have already been described [1]. The method did not change for the ^{11}C Salvinorin B and the ^{11}C EOM-Salvinorin B.

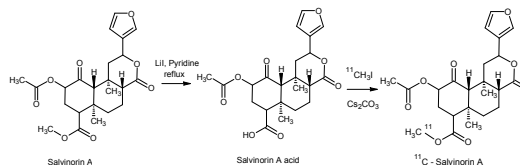


Image analysis: The methods of brain imaging have already been described before [1]. We acquired PET images of the brain and summed the time frames. For the summed time frame of 3-7 minutes we received the following images. Salvinorin A was widely distributed throughout the brain both cortical and sub-cortical regions. The highest ^{11}C concentration at early time points was in the cerebellum. time frames 20-40 minutes. It can clearly be seen that the maximum of the activity is much lower for the Salvinorin B compound. Both compounds have a very short effect on the organism, but since the affinity of Salvinorin B for the receptor is lower than the affinity of Salvinorin A. The effect is much weaker.

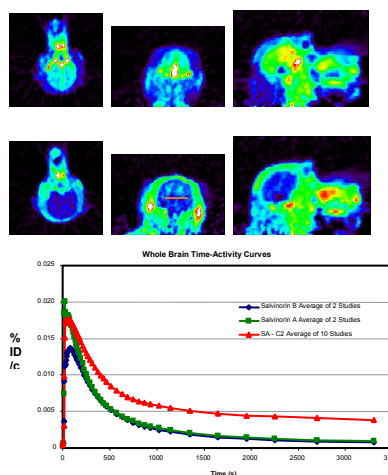


Fig.2: Time activity curve in the ROI of Salvinorin B

In preliminary studies, EOM-Salvinorin B showed similar kinetics. Future studies have to be made. At the interpretation of the PET studies comparing Salvinorin A and Salvinorin B a clear conclusion could be made: The half life of Salvinorin A in the brain was about the same as that of Salvinorin B (see time activity curves). But the maximum activity of Salvinorin A is higher. Furthermore, another study showed that the C2-acetate is metabolised in the organism leading Salvinorin B in vivo. The effect of that can be seen in Fig.2.

In summary, we labelled salvinorin A and salvinorin B at the C-18 position using carbon-11 methylation. Using PET, we demonstrated the rapid entry to and clearance from the brain of both compounds.

Acknowledgement

Funding by DAAD and DOE. Thanks to Jacob Hooker, Frank Rösch (Johannes Gutenberg Universität Mainz), Thomas Munro and Cecile Beguin (McLean Hospital).

References:

- [1] Hooker, J. et al. Pharmacokinetics of the potent hallucinogen, salvinorin A in primates parallels the rapid onset and short duration of effects in humans; *Neuroimage*. 41, 2008 1044-50
- [2] Wuts, P.G.M.; Greene, T.W. *Greene's Protective Groups in Organic Synthesis*, 4th ed.; Wiley: Hoboken, NJ, 2007.
- [3] Munro et al. Standard protecting groups create potent and selective κ opioids: Salvinorin B alkoxyethylethers, *BioorgMed Chem*, 16, 2007; 1279-1286

Radiotracer studies using ^{18}F FDG and $^{11}\text{CO}_2$ as an opportunity for gaining new insights into cellulose synthesis in plants

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Motivation: Developing new technologies enabling the measurement of cellulose rates of formation in plants gives many opportunities for basic research to identify ways in which plant sugars can be manipulated for higher throughput into cell-wall cellulose, a key component of biomass that can be readily converted to biofuel.

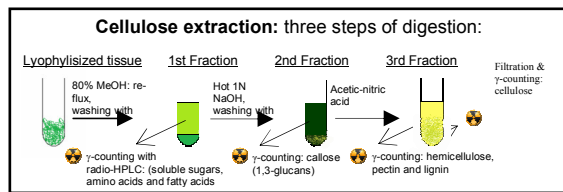
Materials and Approach: Studies were conducted using *Nicotiana tabacum* L (cv Samsun) grown to the 9-leaf stage under a 16/8 light cycle (400 $\mu\text{mol}/\text{m}^2$ s). Two studies were conducted testing the efficacy for using short-lived radioisotopes to measure cellulose rates of formation:

(i) study 1 looked at leaf age, comparing cellulose mass and rates of formation in young apex leaves with older mature leaves;

study 2 looked at the effects of administering a 150 μM solution of the herbicide, isoxaben (ISX). ISX inhibits cellulose production although the mechanism of action is unknown. $^{11}\text{CO}_2$ fed to leaves, is rapidly fixed by the Calvin-Benson Cycle making ^{11}C -sucrose and ^{11}C -starch. ^{11}C -Sucrose can be degraded to ^{11}C -glucose by sucrose synthase where a cellulose synthesizing enzyme stitches the glucose molecules together in a 1,4-glucan change.

We also used ^{18}F FDG, 2-[^{18}F]-fluoro-2-deoxyglucose, a radioactive glucose analog that can be taken up by the roots and transported to leaves where it is used by the plant as a glucose substitute for cell-wall synthesis. The combination of using $^{11}\text{CO}_2$ and ^{18}F FDG tracers gave new insight into the role sugars play in making cellulose.

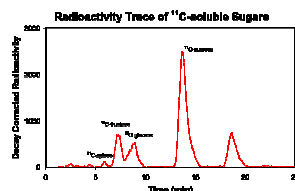
The scheme below outlines 3 extraction steps that were used to rapidly break down plant tissue into cell-wall components. A combination of radio-HPLC analysis and gamma counting gave information of plant carbon partitioning into metabolic pathways:



FDG to the roots

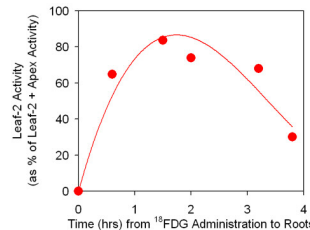
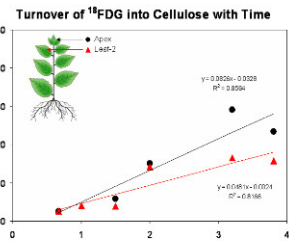
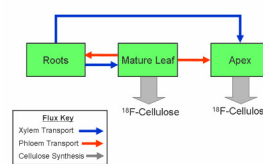
HPLC of first extraction

$^{11}\text{CO}_2$ to the leaves

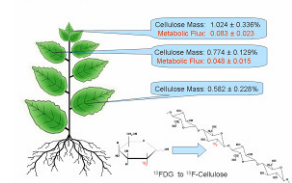


The fragments of the HPLC could be identified as fructose, glucose, sucrose and trehalose.

Compartmental breakdown of ^{18}F FDG transport and metabolism



Tissue Age and Cellulose Turnover

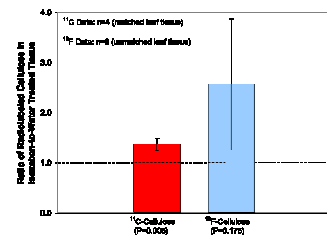


Metabolic flux analysis requires an understanding of the physical transport of tracer into, and out of target tissue over time. Here the amount of ^{18}F FDG in leaf:2 changes over time because sugar can reload into the phloem and export out.

Cellulose mass presented as % gram fresh wt. decreases with leaf age. The rates of cellulose formation as measured by the ^{18}F -cellulose were also found to decrease with leaf age validating the tracer approach.

Isoxaben

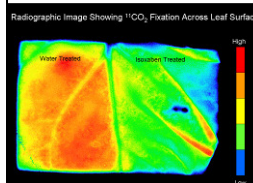
Red: ^{11}C data
 Blue: ^{18}F FDG data



ISX increases metabolic flux of ^{11}C and ^{18}F into cellulose relative to water (control) treatment. ISX decreases radiolabeled sugar specific activities, but for different reasons. For glucose, the ^{11}C pool decreases, but the ^{12}C pool remains unchanged. For sucrose, the ^{11}C pool is unchanged, but the ^{12}C pool increases:

Comparative Ratios of ISX-to-Water Treated Tissue within the Same Leaf

Soluble Sugar	Ratio of Specific Activities in ISX-to-Water	Ratio of [^{11}C]-Sugar Activity in ISX-to-Water	Ratio of [^{12}C]-Sugar Mass in ISX-to-Water	Number of Sample Replicates
Glucose	0.59 ± 0.17	0.57 ± 0.16	0.96 ± 0.11	2
Sucrose	0.58 ± 0.16	0.86 ± 0.13	1.49 ± 0.19	3



ISX decreases photosynthetic activity by $30\% \pm 0.06$ (n=4), relative to controls.

Summary: We believe the effects of ISX are two-fold:

- involving metabolic reprogramming of plant carbon flux between starch and sugar production; and
- inhibiting the sucrose synthase enzyme from degrading plant sucrose to glucose - essentially starving the plant of needed glucose for cell-wall cellulose synthesis.

Acknowledgements: Frank Rösch (Johannes Gutenberg Universität Mainz), Deutscher Akademischer Austauschdienst, Michael Schueller, David Alexoff and Richard Ferrieri

C.

**Radiochemische Analytik für
umweltrelevante und
technische Probleme**

**Radiochemical Analytics for
Environment and Technology**

RIMS, A Suitable Method for Nuclear Forensic Investigations

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Efforts were made in Germany during the Second World War for attaining nuclear energy by a self sustained nuclear chain reaction. In Haigerloch, a little village in the south-west part of Germany, a team of scientists headed by W. Heisenberg tried to reach criticality with a heavy water reactor, the B-8 pile, using 664 metallic uranium cubes suspended from the lid by 76 chains arranged in honey-comb geometry (1.58 t ^{nat}-U) and immersed in 1.71 m³ of heavy water. It was reported that, at the pile's mantle, a neutron multiplication of 6.7 was measured when the B-8 was seeded with neutrons from a (Ra-Be)-source. It is known that the fuel was subject to purification prior to introduction in the reactor, with the intention to eliminate thorium from the matrix. It can be assumed that plutonium would have been also removed by this procedure, provided it was present as Pu(IV).

It is not clear whether the scientists were able to reach criticality with this design. This could be determined, however, by analyzing the nuclear fuel material, by determining the amount of ²³⁹Pu formed as a result of the elevated neutron flux.

Unfortunately, most of the material used for the experiments in the B-8 pile was lost. However, in the 1960's, several cubes of the above mentioned uranium were found. One of them was sent to the Institute for Transuranium Elements, European Commission (ITU). A comprehensive analysis was performed on this material in order to determine its age, the level of impurities, and its origin by the colleagues from ITU. It was found by the uranium/thorium dating technique that the purification took place around September 1943. This indicates that the material could be from the batch used in the Haigerloch reactor.

The isotopic composition of uranium was determined also in Mainz by ICP-MS and indicated just like at ITU the natural composition of uranium (99.27 % ²³⁸U, 0.72 % ²³⁵U, and 0.0055 % ²³⁴U).

Resonance Ionization Mass Spectrometry (RIMS) is an element and isotope selective method and has a very low detection limit for plutonium (LOD ~ 10⁶ atoms). This makes it suitable for analysis of ultra trace amount of plutonium where element and isotopic selectivity is needed.

Therefore, subsamples of the Haigerloch fuel material were analysed by RIMS. For comparison, a sample of uranium ore originating from Joachimsthal and a sample of metallic uranium from the same batch that, however, had not been seeded with neutrons, were investigated. In the first place, the surfaces were etched with 8 M HNO₃ in order to eliminate any possible surface contamination. The samples were then divided into 3 subsamples of ~ 1

g and RIMS filaments were prepared as described in [1]. The content of ²³⁹Pu in the etched material was also determined.

Prior to the RIMS analyses, the efficiency and potential cross contamination of the apparatuses was checked in order to eliminate any suspicions on the accuracy of the measurements. A typical analysis result is shown in Fig. 1.

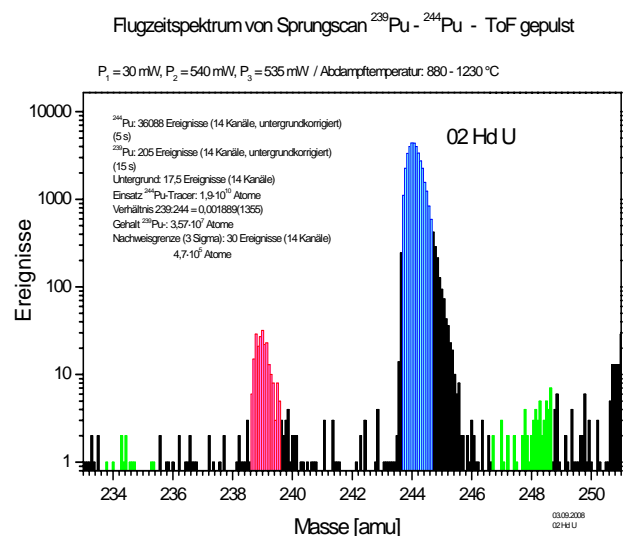


Figure 1. ²³⁹Pu analysis by RIMS. 3*10¹⁰ Atoms ²⁴⁴Pu as tracer

It was found that the amount of ²³⁹Pu in uranium was comparable for all three samples examined at a level of ~ 1.5*10⁻¹⁴ g ²³⁹Pu/ g ²³⁸U. Also, the amount of plutonium found in the material etched from the surface was comparable with the value stated above.

An estimation of the amount of plutonium formed as a result of irradiation by cosmic rays and neutrons resulting from the spontaneous fission of uranium as well as a simulation of the level expected after a potential criticality of the reactor were performed at ITU [2].

After comparing all the experimental results obtained for plutonium with the theoretical simulations, one can conclude that the reactor was not critical.

It can also be stated that RIMS is a suitable method for analyses at ultra trace amounts where high accuracy is needed.

References

- [1] Wunderlich, Th. : Annual Report, Institut für Kernchemie, Universität Mainz, C 19, (2005)
- [2] M. Wallenius et al: to be published

Einrichtung eines neuen Laserlabors für die RIMS und SIMS

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In dem am Institut für Kernchemie angeschlossenen Neubau [1] wurde ein neues Laserlabor eingerichtet. Hier sollen die zukünftigen laserspektroskopischen Untersuchungen an Plutonium, Neptunium und möglichen weiteren Transuranen stattfinden. In nur zwei Monaten wurden aus den Kellern des nicht mehr sanierungsfähigen Gebäudes M-Haupt des Fachbereichs Chemie [2], die Apparaturen der Laserlabore abgebaut, in den Neubau transportiert und dort mit wesentlichen Verbesserungen wieder aufgebaut.



Abb. 1: Der alte Lasertisch im alten Keller der Kernchemie im Universitätsgebäude M-Haupt

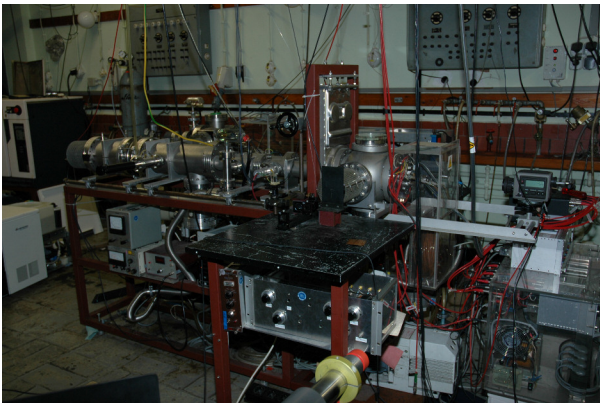


Abb. 2: Der TOF-MS Aufbau im Keller daneben

Das komplette Lasersystem bestehend aus einer neuen Nd:YAG Laserpumpe der Firma Photonics Industries, welche den alten Pumplaser ORC-1000, Clark Ind. ersetzt, drei Ti:Sa-Laser und die gesamte, vollständig erneuerte, Strahlführung wurden auf einem neuen Lasertisch montiert. Die gesamte Elektronik wurde in einem neu angeschafften Elektronikschrank untergebracht. Das zukünftige Datenverarbeitungssystem der RIMS soll darin ebenfalls seinen Platz finden. Sämtliche elektrischen Anschlüsse, Verkabelungen und Datenleiter (mehr als 200 m) wurden mit Hilfe der Elektronikwerkstatt des Instituts überprüft, teilweise ersetzt und neu verlegt. Dies ermöglicht ein sichereres, zuverlässigeres und

rationelleres Arbeiten. Für das TOF-Massenspektrometer wurden zwei neue Drehschiebervakuumpumpen angeschafft. Die vorher teils problematische Kühlung der gesamten Apparatur wurde ebenfalls modernisiert. Dabei wurden mehr als 100 m Schlauch verlegt.



Abb. 3: Das neue Laserlabor im Neubau Kernchemie, sichtbar sind der neue Lasertisch, der neue Elektronikschrank und das (alte) TOF-MS



Abb. 4: Das neue Lasersystem in Betrieb

Ebenfalls Platz fanden eine Beschichtungsanlage für Filamente, welche in der RIMS eingesetzt werden und eine TOF-SIMS-Apparatur für zukünftige Forschungsarbeiten mit heißen Mikropartikeln, sogenannten „Hot Particles“.

Literatur:

- [1] Homepage des Landesbetrieb LBB Rheinland-Pfalz, Hochtechnologiegebäude für die Kernchemie der Johannes Gutenberg-Universität Mainz
- [2] S. Rathjen, Kernchemie zieht in Neubau ein, Allgemeine Zeitung, (28. 10. 2008)

Danksagung:

Diese Arbeit wurde finanziell unterstützt vom DFG-Graduiertenkolleg der Uni Mainz, GRK 826 und vom BMWi, Förderkennzeichen 02E10166

Neptunium(V) diffusion in Opalinus Clay

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Argillaceous rocks are considered in several countries, including Germany, as potential host rock for the construction of repositories for high-level radioactive waste. Opalinus Clay (OPA) is currently investigated as a candidate host rock formation for the Swiss nuclear waste repository because of the very low hydraulic conductivity ($10^{-14} \text{ m/s} < K_h < 10^{-13} \text{ m/s}$) and high sorption ability of OPA. Diffusion is considered to be the dominating processes governing the transport of radionuclides in clay. To better understand the diffusion behavior of Np(V) in OPA, in-diffusion experiments with an abrasive peeling technique [1] were performed under ambient conditions using synthetic pore water (pH 7.6) as mobile phase.

The in-diffusion set-up is described in [2]. OPA (BAE-25/10, 25.4 F x 11 mm) used was from Mont Terri without special pre-treatment. Pore water was spiked with $^{237}\text{Np(V)}$ and $^{22}\text{Na}^+$. $^{22}\text{Na}^+$ was used to check the reliability of the in-diffusion technique. The abrasive peeling technique [1] was used to determine the concentration profile of ^{237}Np in OPA. The activities were measured directly by γ -ray spectroscopy using the γ -lines of ^{237}Np at 29.37 and 86.48 keV and of ^{22}Na at 1274.5 keV, respectively.

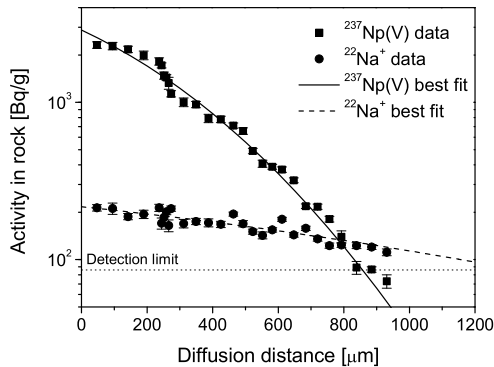


Figure 1. Concentration profile of ^{237}Np and ^{22}Na in OPA (Mont Terri) under ambient conditions. Synthetic pore water (pH 7.6) was the mobile phase.

The analysis of the experimental data (Fig. 1) assumed a single reservoir with decreasing concentrations for ^{237}Np and ^{22}Na due to in-diffusion into a semi-infinite sample [3]. An in-house computer code was used to obtain the effective diffusion coefficient D_e and the rock capacity factor α from the experimental data. The distribution ratio K_d was deduced using the relationship $\alpha = \varepsilon + \rho \cdot K_d$, where the porosity ε was measured by a through-diffusion experiment with HTO.

The quality of the diffusion parameters D_e and α was tested by using them as input parameters for the calculation of the radionuclide concentrations in the source reservoir (Fig. 2).

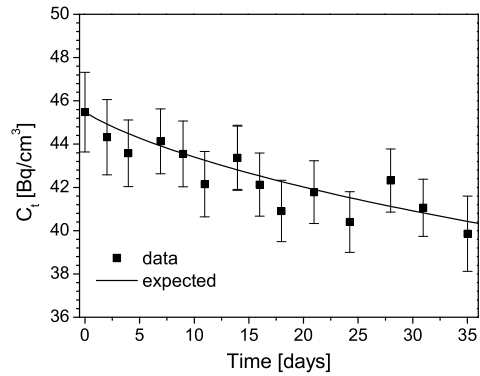


Figure 2. Concentration of ^{237}Np in the source reservoir as a function of time.

The results of the in-diffusion-experiment and the parameters used to reproduce the experimental data for $^{237}\text{Np(V)}$ and $^{22}\text{Na}^+$ are summarized in Table 1.

Table 1. Diffusion parameters for ^{237}Np and ^{22}Na

	$^{237}\text{Np(V)}$	$^{22}\text{Na}^+$
C_0 (Bq/m ³)	$(45.5 \pm 1.8) \times 10^6$	$(1.00 \pm 0.05) \times 10^9$
V (ml)	210	20
t (s)	3.1×10^6	6.1×10^4
ρ (kg/m ³)	2420 ± 8	2420 ± 8
d (cm)	2.54 ± 0.01	2.54 ± 0.01
l (cm)	1.10 ± 0.01	1.10 ± 0.01
P_b (m/s)	$(3.8 \pm 0.7) \times 10^{-8}$	-
l_b (mm)	1.57 ± 0.01	-
ε	0.15 ± 0.01	0.15 ± 0.01
D_e (m ² /s)	$(6.9 \pm 1.1) \times 10^{-12}$	$(1.8 \pm 0.2) \times 10^{-11}$
α	243 ± 4	0.44 ± 0.03
K_d (m ³ /kg)	$(10.0 \pm 1.0) \times 10^{-2}$	$(1.4 \pm 0.1) \times 10^{-4}$

In order to study the diffusion behavior of $^{237}\text{Np(V)}$ in OPA under reduction conditions, future diffusion experiments will be carried out under an argon atmosphere.

Acknowledgments

The authors would like to thank Ch. Marquard (FZK) for providing OPA. This work was supported by the BMWi grant No. 02E10166

References

- [1] Van Loon, L.R. et al., Appl. Radiat. Isotopes 63, 11 (2005)
- [2] Van Loon, L.R. et al., Environ. Sci. Technol. 42, 1600 (2004)
- [3] Yaroshchuk, A.E. et al., J. Contam. Hydrol. 97, 67 (2008)

Sorption von Np(V) an Opalinuston in Abhängigkeit der Tonmenge, der Np-Konzentration und des pH-Wertes

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Tongestein wird in verschiedenen Ländern, unter anderem auch in Deutschland und der Schweiz, als potentielles Wirtsgestein für die Endlagerung hoch radioaktiver Abfälle diskutiert. Opalinuston (OPA), der unter anderem im Zürcher Weinland in der Schweiz vorkommt, wurde dabei als Referenzton für die Untersuchung des Migrationsverhaltens von Radionukliden im Gestein und dem umgebenden Grundwasser mit Hinblick auf den Sicherheitsnachweis für ein nukleares Endlager ausgewählt.

Neptunium wird durch sein langlebiges Isotop Np-237 ($t_{1/2} = 2,1 \cdot 10^6$ a) einen wesentlichen Beitrag zur Radiotoxizität der abgebrannten Brennelemente liefern und muss daher in solchen Sicherheitsbetrachtungen Berücksichtigung finden.

Ziel dieser Studie war es, das Sorptionsverhalten von Np(V) an OPA (Mont Terri, Schweiz, BHE-241) in Abhängigkeit verschiedener Parameter zu untersuchen. Um eine Auflösung des im Opalinuston enthaltenen Calcits (etwa 15 %) zu vermeiden, wurden alle Experimente in Calcit-Lösung (gesättigt an Luft beim jeweiligen pH-Wert) durchgeführt. Verschiedene Np-Konzentrationen wurden durch Zugabe unterschiedlicher Mengen Np-237- und Np-239-Lösung eingestellt.

Durch Variation der Tonmenge zwischen 2 und 20 g/l ($[Np] = 8 \cdot 10^{-6}$ mol/l) und der Np-Konzentration zwischen 10^{-4} und 10^{-12} mol/l ($[OPA] = 15$ g/l), jeweils in an Luft gesättigter Calcit-Lösung (pH = 8,23), wurden Sorptionsisothermen (doppeltlogarithmische Auftragung der sorbierten Np-Menge Γ in mol/kg gegen die Np-Konzentration im Gleichgewicht $[Np]_{eq}$ in mol/l) aufgestellt. Diese sind in Abb. 1 dargestellt.

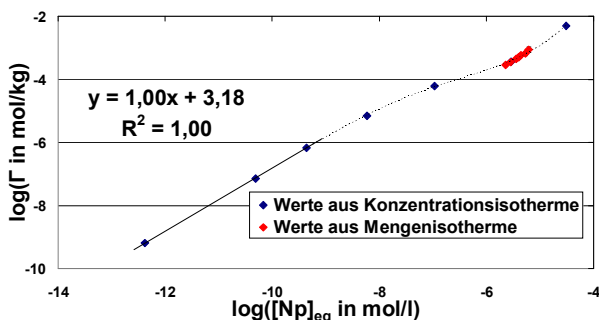


Abb. 1: Isotherme für die Sorption von Np(V) an OPA bei pH 8,2

Im Bereich niedriger Np-Konzentrationen zeigt die Kurve Freundlich-Verhalten mit einer Steigung von Eins. Der Verteilungskoeffizient ($K_d = \Gamma/[Np]_{eq}$) in diesem Bereich ergibt sich demnach aus dem Achsenabschnitt der dargestellten Regressionsgeraden ($K_d = 1524$ l/kg).^[1] Bei höheren Np-Konzentrationen von ca. 10^{-5} mol/l geht die Kurve in einen zweiten linearen Bereich. Dies ist wahrscheinlich auf Sorptionsstellen unterschiedlich hoher Affinität

bezüglich Np zurückzuführen,^[2] wobei im Bereich hoher Np-Konzentrationen die Stellen mit hoher Affinität komplett belegt sind und die Besetzung der Sorptionsplätze geringerer Affinität zu einem kleineren K_d -Wert führt.

Der Einfluss des pH-Wertes wurde im Bereich zwischen pH = 6 und 10 für verschiedene Np-Konzentrationen zwischen 10^{-5} und 10^{-12} mol/l untersucht. Das Feststoff/Lösung-Verhältnis betrug dabei 15 g/l. In Abb. 2 ist die pH-Abhängigkeit des K_d graphisch dargestellt.

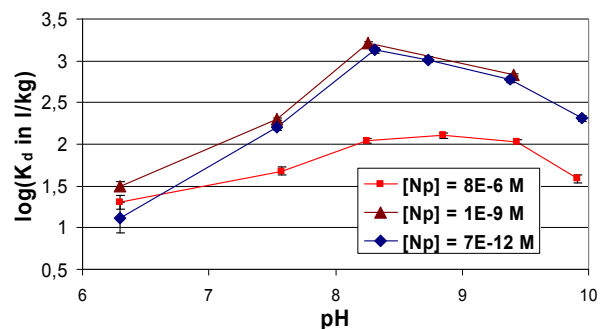


Abb. 2: pH-Abhängigkeit des K_d für die Sorption von Np(V) an OPA

Die Sorption wird zwischen pH = 8 und 9 maximal und sinkt zu höheren pH-Werten in Folge stärker ausgeprägter Carbonat-Komplexierung ab.^[3] Mit sinkender Np-Konzentration steigen die prozentuale Sorption und damit der K_d -Wert aufgrund des größeren Angebots an Sorptionsplätzen mit hoher Affinität stark an. Im Sorptionsmaximum steigt der K_d -Wert um eine ganze Größenordnung. In Übereinstimmung mit der Sorptionsisotherme (Abb. 1) ändert sich im Konzentrationsbereich zw. 10^{-9} und 10^{-12} mol/l der K_d für die Sorption von Np(V) an OPA praktisch nicht.

Literatur:

- [1] D. Langmuir, *Aqueous Environmental Geochemistry*, Upper Saddle River: Prentice Hall, 1997, 355-361.
- [2] C. Poinssot et al., *Geochim. Cosmochim. Acta*, 1999, 63, 3217-3227.
- [3] V. Neck et al., *Radiochim. Acta.*, 1994, 65, 29-37.

Diese Arbeit wurde finanziert durch das Bundesministerium für Wirtschaft und Technologie (Förderkennzeichen 02E10166).

Sorption von Np(V) an Opalinuston unter aeroben/anaeroben Bedingungen und Berücksichtigung von Huminsäure

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Viele Studien haben gezeigt, dass organische Moleküle einen deutlichen Effekt auf das Sorptionsverhalten von Radionukliden haben.^[1] Bei der Sicherheitsbetrachtung und Planung eines Endlagers für hoch radioaktive Abfälle müssen daher unbedingt organische Substanzen, die beispielsweise im Boden und auch in Tonen wie dem Opalinuston (OPA), die als mögliches Wirtsgestein diskutiert werden, vorkommen berücksichtigt werden.

Als Modellsubstanz zur Untersuchung dieser Effekte diente in dieser Studie synthetische C-14-markierte Huminsäure (HS) vom Typ [¹⁴C]M42 verwendet.^[2] Die pH-Abhängigkeit der Sorption von Np(V) an OPA (15 g/l) wurde bei verschiedenen Np-Konzentrationen (8 µM und 7 pM) in An- und Abwesenheit von HS (10 mg/l) sowohl unter aeroben als auch anaeroben Bedingungen untersucht.

Die Np-Konzentration wurde durch entsprechende Zugabe von Np-237- und Np-239-Lösungen eingestellt und die HS wurde bei den entsprechenden Experimenten unmittelbar vor dem Np zugegeben.

Die aeroben Experimente wurden an Luft mit aerob aufbereitetem Opalinustonpulver (BHE-241) in Calcit-Lösung, die beim jeweiligen pH gesättigt war, durchgeführt. Die Experimente unter anaeroben Bedingungen wurden ebenfalls in mit Calcit gesättigter Lösung durchgeführt; allerdings mit anaerobem Opalinustonpulver (BDR 2) und unter erhöhtem CO₂-Partialdruck (p_{CO₂} = 10^{-2,3} atm), wie er in der Tonformation angenommen wird.^[3]

In Abb. 1 sind die Ergebnisse der Messungen an Luft aufgetragen. Die Kurven mit HS sind dabei jeweils durchgezogen, die Kurven bei niedriger Np-Konzentration (7 pM) rot dargestellt.

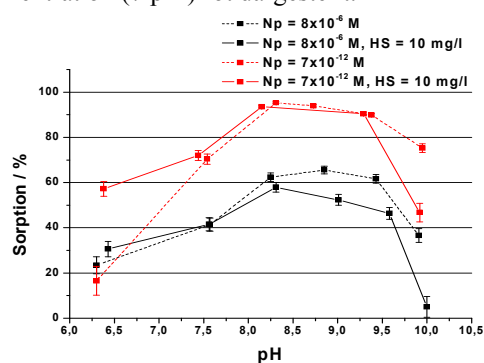


Abb. 1: Sorption von Np(V) an OPA unter aeroben Bedingungen in An- und Abwesenheit von HS

Man erkennt, dass die Huminsäure bei pH 10 einen mobilisierenden Effekt auf Np(V) hat. Dies ist wahrscheinlich auf die Bildung von Humat- oder ternären Humat-Carbonat-Komplexen

zurückzuführen.^[4] Zwischen pH 7,5 und 9,5 ist nur bei 8 µM Np ein geringfügiger Effekt sichtbar. Unter anaeroben Bedingungen (siehe Abb. 2) ergibt sich ein anderes Bild.

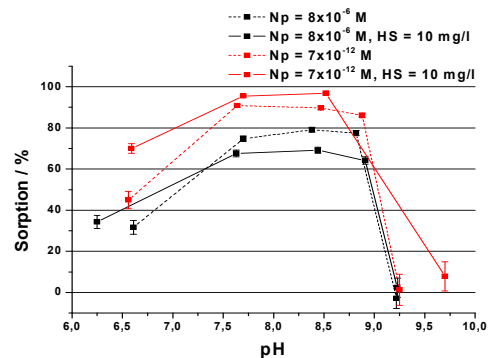


Abb. 2: Sorption von Np(V) an OPA unter anaeroben Bedingungen in An- und Abwesenheit von HS

Zwischen pH 7 und 9 wird Np deutlich stärker sorbiert als an Luft, was durch die mittels Flüssig-flüssig-Extraktion nachgewiesene Reduktion von Np(V) zu Np(IV) und die stärkere Sorption von Np(IV) erklärt werden kann.

Aufgrund des höheren CO₂-Partialdruckes und der daraus resultierenden höheren Carbonat-Konzentration dominiert die Komplexbildung von Np mit Carbonat und die Wechselwirkung mit Huminsäure ist entsprechend schwächer ausgeprägt. Die höhere Carbonat-Konzentration ist auch Grund für die starke Abnahme der Sorption bei pH > 9.

Zusammenfassend kann gesagt werden, dass Huminsäure nur im alkalischen pH-Bereich einen mobilisierenden Effekt auf Np(V) hat, der mit steigender Np-Konzentration stärker ausgeprägt ist. Unter anaeroben Bedingungen wird Np(V) zu Np(IV) reduziert, wodurch Np zwischen pH 7 und 9 stärker sorbiert. Durch Erhöhung des CO₂-Partialdruckes verliert Huminsäure an Einfluß auf die Sorption und es dominiert die Carbonat-Komplexierung.

Literatur:

- [1] Y. Niitsu et al., *J. Nucl. Mater.*, **1997**, 248, 328-332.
- [2] S. Pompe et al., *Wiss.-Techn. Bericht, FZD-290*, Forschungszentrum Dresden-Rossendorf, **2000**.
- [3] M.J. Turrero et al., *J. Iberian Geol.*, **2006**, 32, 233-258
- [4] S. Sachs et al., *Wiss.-Techn. Bericht FZD-460*, Forschungszentrum Dresden-Rossendorf, **2007**.

Diese Arbeit wurde finanziert durch das Bundesministerium für Wirtschaft und Technologie (Förderkennzeichen 02E10166).

Untersuchung von Plutonium unter anaeroben und aeroben Bedingungen

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Für die Analyse und Speziation des Plutoniums unter umweltrelevanten Bedingungen wurde die Kapillarelektrophorese (CE) angewandt, welche an ein Inductively-Coupled-Plasma-Mass-Spektrometer (ICP-MS) gekoppelt wurde.

Die Systeme Pu/HNO₃ (pH 0,9), Pu/NaClO₄ (pH 7,6) und Pu/Porenwasser (pH 7,6) wurden unter aeroben und anaeroben Bedingungen analysiert. Die verschiedenen Plutoniumspezies wurden elektrolytisch (Pu(III), Pu(IV)) und auf nasschemischem Weg (Pu(VI)) jeweils frisch vor der Verwendung hergestellt und mit UV/VIS-Spektroskopie überprüft. Dann erfolgte die Zugabe zu den entsprechenden Lösungen (0,2 M HNO₃, 0,4 M NaClO₄ und Porenwasser) an Luft bzw. unter Argonatmosphäre und das Nachstellen des pH-Wertes. Nach 5 Tagen wurden die pH/Eh-Werte erneut gemessen und die einzelnen Lösungen mit CE-ICP-MS untersucht.

Die Abbildungen 2 und 3 zeigen Eh-pH-Diagramme (die rote Linie entspricht der Phasengrenze Pu(V)/Pu(IV) neueren Ursprungs [2]) mit den Messpunkten für die aeroben und anaeroben Proben. In allen Fällen lag in 0,2 M HNO₃ nur Pu(III) vor.

Stammleg.	0,2 M HNO ₃	0,4 M NaClO ₄	Porenwasser
Pu(III)	●	●	●
Pu(V)	■	■	■
Pu(VI)	◆	◆	◆

Abb. 1: Legende für die Messwerte in den Eh-pH-Diagrammen

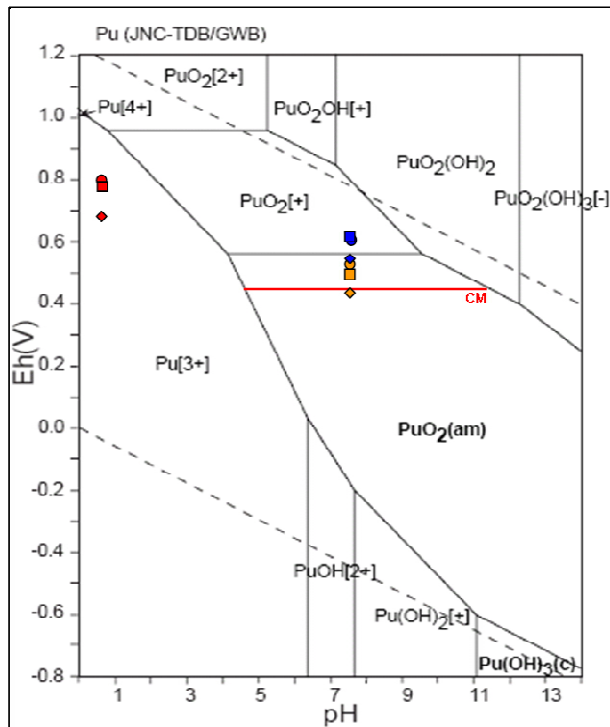


Abb. 2: Eh-pH-Diagramm [1] von Pu in wässriger Lösung, Messwerte unter aeroben Bedingungen

Unter aeroben Bedingungen findet sich in NaClO₄ nur Pu(V). In Porenwasser ist ebenfalls fast ausschließlich Pu(V) stabil, wenig Pu(IV) konnte nachgewiesen werden. Dies ist in guter Übereinstimmung mit Vergleichsdaten aus der Literatur.

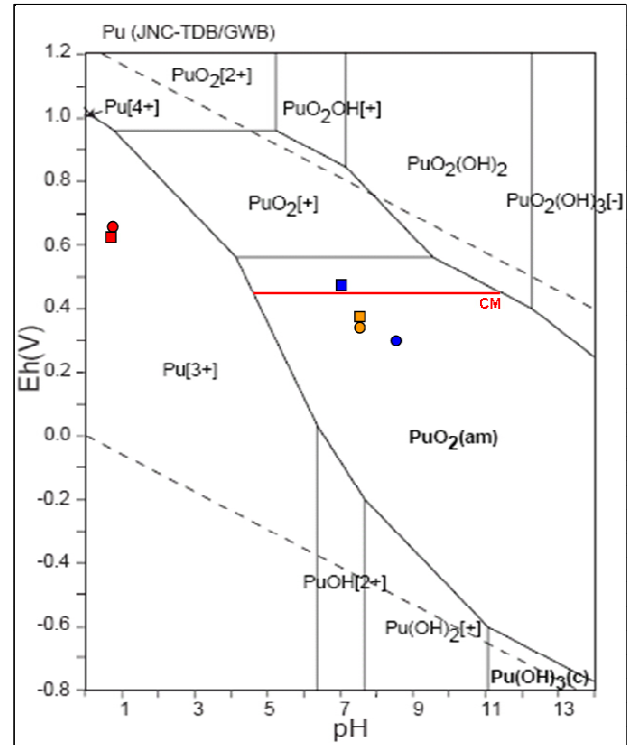


Abb. 3: Eh-pH-Diagramm [1] von Pu in wässriger Lösung, Messwerte unter anaeroben Bedingungen

Unter anaeroben Bedingungen konnte in 0,4 M NaClO₄ eine Mischung aus Pu(V) und Pu(VI) nachgewiesen werden. Für das Medium Porenwasser stellte sich heraus, dass einzig Pu(V) als stabiler Oxidationszustand nachgewiesen werden konnte. Dies ist nicht im Einklang mit den dargestellten Diagrammen, dennoch gibt es in der Literatur publizierte Daten, die diese Ergebnisse stützen, da sich die gemessenen Werte in einem Grenzbereich zwischen zwei Phasen befinden. Die Genauigkeit einer Redox-Potentialmessung lag bei den durchgeführten Versuchen bei ≈ 50 mV. Die durchgeführten Arbeiten sollen die Datenbasis für Plutonium erweitern.

Literatur:

- [1] N. Takeno, Atlas of Eh-pH diagrams, Intercomparison of thermodynamic databases, Geological Survey of Japan Open File Report No. 419 (2005)
- [2] C. Marquardt et al., Actinide redox chemistry – Pu in clay, Presentation 5th BMWi-Workshop Speyer (2008)

Danksagung:

Diese Arbeit wurde finanziell unterstützt von ACTINET und vom BMWi, Förderkennzeichen 02E10166

Bestimmung des Verteilungskoeffizienten von Pu im System Pu/Porenwasser/Opalinuston unter anaeroben Bedingungen

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Es wurde die Sorption von Pu an Opalinuston in Porenwasser unter umweltnahen Bedingungen untersucht. Dabei wurden die K_d -Werte der anaeroben Sorption von Pu(III) und Pu(IV) an Opalinuston mittels Freundlich-Isotherme bzw. Berechnung des K_d -Wertes für jeden Datenpunkt bestimmt [1].

Die Experimente für die Spezies Pu(III) und Pu(IV), sowie alle nötigen Vorbereitungen, wurden unter Luftausschluss in Argonatmosphäre und einem Partialdruck von $p(\text{CO}_2) = 10^{-2,3}$ atm durchgeführt. Das Lösungsmittel war synthetisches Porenwasser, pH 7,6 [2].

Die Probengefäße wurden mit Milliporewasser gespült und an Luft bzw. unter Argonatmosphäre getrocknet. Dann erfolgte die Einwaage der entsprechenden Mengen Opalinuston. Danach wurde der Ton mit Porenwasser kontaktiert und konditioniert. Nach 72 h wurden die entsprechenden Plutoniumspezies zugegeben und der pH-Wert mit NaOH bzw. HCl auf 7,6 nachgestellt. Die Sorptionsstammlösungen des Plutoniums wurden direkt vor der Verwendung elektrolytisch hergestellt und mittels UV/VIS-Spektroskopie überprüft. Dann wurden wieder 72 Stunden bis zur Gleichgewichtseinstellung gewartet. Die Proben wurden dabei ständig geschüttelt. Die Phasentrennung erfolgte durch Zentrifugieren bei 81,769 g über 1 h. Die aus der flüssigen Phase entnommenen Aliquoten wurden mittels LSC auf den Plutoniumgehalt analysiert und daraus, wie vorher erwähnt, der Verteilungskoeffizient K_d berechnet.

Die Versuche wurden durch die Variation der Opalinustonmenge zwischen 0,17 - 10,0 g/L und bei konstanter Plutoniumkonzentration (Pu(III) $\approx 0,09 \mu\text{M}$, Pu(IV) $\approx 0,09 \mu\text{M}$) durchgeführt. Die Wandabsorption des Plutoniums an den Reaktionsgefäßen beträgt unter den Reaktionsbedingungen ohne Zugabe des Tonminerals über 90% für Pu(IV) und Pu(III). Schon bei geringen Mengen von Opalinuston werden jedoch 97% des Plutoniums an dem Tongestein sorbiert (0,166 g/l für Pu(IV) bzw. Pu(III)).

In den Abbildungen 1 und 2 ist der Logarithmus des Verteilungskoeffizienten K_d in Abhängigkeit des Logarithmus der Plutoniumkonzentration im Gleichgewicht für Pu(III) und Pu(IV) dargestellt.

Die K_d -Werte sind wie folgt: $K_d = 114 \text{ m}^3/\text{kg}$ für Pu(III) und $K_d = 178 \text{ m}^3/\text{kg}$ für Pu(IV).

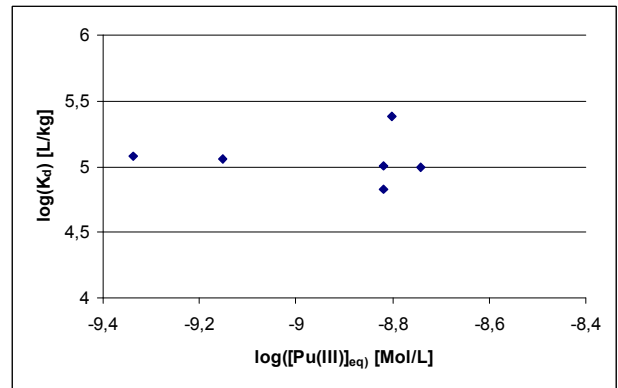


Abb. 1: Logarithmus K_d in Abhängigkeit des Logarithmus $[\text{Pu}]_{\text{eq}}$ im Gleichgewicht für Pu(III)

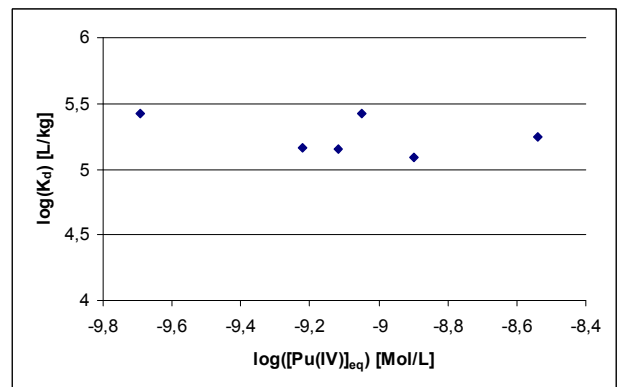


Abb. 2: Logarithmus K_d in Abhängigkeit des Logarithmus der $[\text{Pu}]_{\text{eq}}$ im Gleichgewicht für Pu(IV)

Diese Werte zeigen, dass Plutonium unter den gewählten umweltnahen Bedingungen sehr stark an Opalinuston sorbiert. Obwohl von der drei- bzw. vierwertigen Plutoniumspezies im Experiment ausgegangen wurde, gibt es Hinweise darauf, dass das Plutonium unter den gewählten Bedingungen als fünfwertige Spezies in der Lösung vorliegt. Weitere Details finden sich im Jahresbericht [3]. Zur Zeit werden mehrere Proben mit der CE-RIMS auf ihre Spezieszusammensetzung untersucht.

Literatur:

- [1] D. Langmuir, Aqueous Environmental Chemistry, ISBN 0-02-367412-1 (1997)
- [2] L.R. Van Loon et al., Diffusion of HTO, ^{36}Cl and ^{125}I in Opalinus Clay samples from Mont Terri: Effect of confining pressure, Journal of Contaminant Hydrology 61 (2003)
- [3] T. Wunderlich et al., Untersuchung von Plutonium unter anaeroben und aeroben Bedingungen, Institut für Kernchemie, Jahresbericht (2008)

Danksagung:

Diese Arbeit wurde finanziell unterstützt vom BMWi, Förderkennzeichen 02E10166

Synthesis and characterization of sulfur-containing humic acid model substances

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Introduction: Depending on their origin, humic substances contain different amounts of sulfur ranging from 0.1 to 3.6% and 0.5 to 1.43% in soil and aquatic humic substances, respectively [1]. Reduced (e.g., sulfides, disulfides, thiols, thiophenes), intermediately oxidized (e.g., sulfoxides, sulfonates) and highly oxidized (e.g., sulfates) sulfur functionalities occur in humic substances [2]. However, their importance for the metal ion complexation by humic substances is still unclear. Sulfur-containing humic acid model substances have been synthesized and characterized for the study of the influence of sulfur functionalities on the metal ion complexation by humic substances.

Experimental: The synthesis of sulfur-containing humic acids type M1-S was performed in aqueous solution based on the synthesis of humic acid type M1 [3]. Syntheses starting from xylose (2.83 M), phenylalanine (0.76 M) and varying amounts of glycine and cysteine were performed. The initial concentration of cysteine was increased from 0 to 0.83 M to obtain humic acids with different sulfur contents. In parallel, the glycine concentration was reduced for the same amount from 0.83 to 0 M, ensuring constant amino acid concentrations in the synthesis mixtures. The resulting synthetic products were characterized for their elemental composition, structure and functionality by elemental analysis, FTIR spectroscopy and potentiometric titration, respectively. First X-ray photoelectron spectroscopy (XPS) measurements of humic acid M1-S-1 were performed in comparison to L-cysteine to identify sulfur species in the synthetic product.

Results: Table 1 shows sulfur content and proton exchange capacity (PEC) of the synthesized humic acids. Both, sulfur content and PEC increases with increasing initial cysteine concentration in the reaction mixtures. However, independent of the sulfur content, all synthetic products show comparable FTIR spectra (not shown) indicating similar overall structures. No FTIR absorption bands pointing to sulfur-containing functional groups were observed in the FTIR spectra. This is attributed to the low sulfur content of the humic acids and the overlapping of IR absorption bands of sulfur functionalities with those of other structural elements of the humic acids.

Table 1. Sulfur content and proton exchange capacity (PEC) of humic acid model substances synthesized with varying cysteine concentrations.

HA	[Cysteine] ₀ (M)	S (%)	PEC (meq/g)
M1	0	0	1.56 ± 0.13
M1-S-1	0.26	1.94 ± 0.01	1.63 ± 0.16
M1-S-2	0.57	3.94 ± 0.04	1.90 ± 0.17
M1-S-3	0.83	7.72 ± 0.05	2.71 ± 0.13

Figure 1 shows the S 2p XPS spectrum of humic acid M1-S-1. In this spectrum two components were detected indicating the occurrence of at least two different sulfur

species in humic acid M1-S-1. Table 2 summarizes the S 2p binding energies of L-cysteine and humic acid M1-S-1.

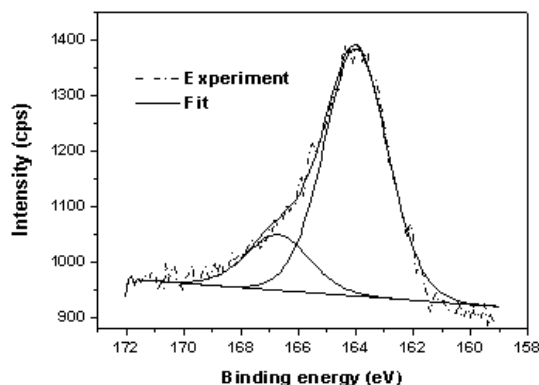


Figure 1. S 2p XPS spectrum of humic acid M1-S-1.

Table 2. S 2p binding energies of cysteine and humic acid M1-S-1 in eV. Electrostatic charging of the sample surface was corrected by setting the C 1s binding energy of M1-S-1 to 285.0 eV.

	S 2p binding energy (eV)	
L-cysteine	163.8	-
M1-S-1	164.0	166.7

Based on literature data [4] and on the binding energy of cysteine, an assignment of the binding energies of humic acid M1-S-1 to different sulfur species was performed. The XPS signal at 164.0 eV can be retained to reduced sulfur species such as thiols, dialkylsulfides and/or disulfides. About 82% of sulfur in humic acid M1-S-1 occurs in this reduced form. The binding energy at 166.7 eV is attributed to sulfoxides, representing about 18% of the sulfur species. From that it is concluded that the main part of sulfur groups in humic acid M1-S-1 occurs in reduced form which is due to the use of L-cysteine as precursor.

Further XPS measurements are performed to characterize the sulfur species in the humic acid model substances with higher sulfur content. The results will be compared to those of natural humic acids. Furthermore, the newly developed sulfur-containing humic acid model substances are used in complexation studies with uranium(VI) to determine the influence of the identified sulfur species on the uranium(VI) complexation by humic acids. The results will be used to assess the impact of sulfur-containing humic acid functionalities on the uranium(VI) complexation by humic acids in comparison to oxygen and nitrogen functionalities.

References

- [1] Xia K., et al. (1998) Soil Sci Soc. Am. J. 62, 1240-1246.
- [2] Solomon D., et al. (2003) Soil Sci Soc. Am. J. 67, 1721-1731.
- [3] Pompe S., et al. (1996) Radiochim. Acta 74, 135-140.
- [4] Lindberg B.J., et al. (1970) Phys. Scripta 1, 286-298.

Acknowledgement

This work was financially supported by BMWi grants 02E10156 and 02E10166.

CE-(DAD)-ICP-MS zur Bestimmung der Komplexbildungskonstanten für die Komplexierung von Lanthanoiden mit Huminsäure

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In den bereits bestehenden Aufbau der CE-DAD-ICP-MS-Kopplung wurde ein neues Zerstäubersystem integriert. Mit diesem Kopplungssystem wurden Komplexbildungskonstanten ($\log \beta$) für die Komplexierung von Lanthanoiden mit Huminsäure bestimmt.

In früheren Arbeiten konnte die grundsätzliche Eignung der CE-DAD-ICP-MS-Kopplung^[1] beziehungsweise CE-ICP-MS-Kopplung^[2,3] für die Bestimmung von $\log \beta$ -Werten unter Beweis gestellt werden. Dazu werden mittels Kapillarelektrophorese (CE) die freien von den komplexierten Metallionen getrennt und die einzelnen Spezies mittels Dioden-Array-Detektor (DAD) und Massenspektrometrie mit induktiv gekoppeltem Plasma (ICP-MS) detektiert. Ausgehend von den Anteilen an freiem und gebundenem Metall wird $\log \beta$ nach dem „metal ion charge neutralisation model“ (CNM)^[4] berechnet.

Für die Kopplung des Kapillarelektrophorese-Systems „ α -CENTAURI NG“ mit der ICP-MS „7500ce“ der Firma Agilent wurde ein „total consumption“-Zerstäuber „MiraMist CE“ der Firma Burgener Research angeschafft. Das Prinzip der Kopplung ist gleich dem etablierten System^[1], jedoch wird hier der Zusatzelektrolyt nicht vom Zerstäuber selbst angesaugt, sondern mittels einer Spritzenpumpe zugeführt. Im Vergleich zu anderen Zerstäubern ist für die Zerstäubung eine wesentlich geringere Flüssigkeitsmenge ($\leq 10 \mu\text{L}/\text{min}$) notwendig. Das Aerosol, und somit der Analyt, wird vollständig ins Plasma überführt. Auf diese Weise kann eine Steigerung der Nachweispflichtigkeit erreicht werden. Abbildung 1 zeigt schematisch den Aufbau der CE-ICP-MS-Kopplung mit dem neuen Zerstäubersystem.

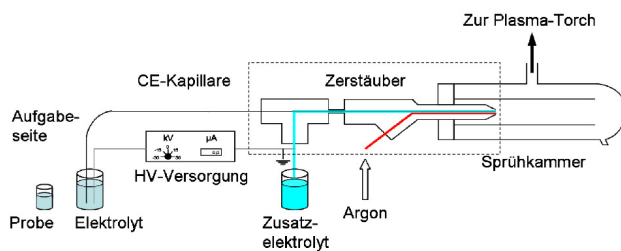


Abbildung 1. Schematischer Aufbau der CE-ICP-MS-Kopplung mit „MiraMist CE“-Zerstäuber

Zur Bestimmung von $\log \beta$ muss ein Korrekturfaktor, die „loading capacity“ LC, für die vorgegebenen Reaktionsbedingungen (pH, Ionenstärke, Art der Huminsäure) bekannt sein oder experimentell ermittelt werden. Zur Bestimmung der LC wurden bei konstanter Huminsäurekonzentration (100 ppm) unterschiedliche Mengen an Holmium (10 ppb bis 5 ppm) zugesetzt. Der pH-Wert (4,3) sowie die Ionenstärke (0,1 M; NaClO_4) wurden bei allen Proben dieser Messreihe konstant

gehalten. Die Trennungen selbst wurden ebenso unter jeweils gleichen Bedingungen (Acetatpuffer (0,1 M Essigsäure, 0,01 M Natriumacetat; pH 3,7) als Elektrolyt, Trennungsspannung 30 kV, Trenndruck 250 mbar) durchgeführt.

Durch Integration des neuen Zerstäubersystems konnte eine Steigerung der Empfindlichkeit der CE-ICP-MS-Kopplung um eine Größenordnung erreicht werden.

Die Bestimmung des LC-Wertes ist mit dem vorhandenen System nur bedingt möglich. Hier zeigte sich eine deutliche Abweichung vom erwarteten Wert. Die Trennung der einzelnen Spezies konnte noch nicht optimiert werden. Dadurch ist es nicht möglich in einem zur Bestimmung des LC-Wertes geeigneten Bereich des Konzentrationsverhältnisses von Metall zu Huminsäure (hohe Beladung) die Anteile an komplexiertem und freiem Metall zu bestimmen. Bei der Optimierung der Trennparameter müssen daher noch weitere Arbeiten geleistet werden.

Über die alternativ mit Ultrafiltration und ICP-MS bestimmte pH-Abhängigkeit des LC-Wertes der Aldrich-Huminsäure konnte ein den Bedingungen entsprechender LC-Wert abgeschätzt werden. Die damit ermittelte Komplexbildungskonstante $\log \beta$ ($6,01 \pm 0,26$) fügt sich sinnvoll in die Reihe der bereits in der Literatur beschriebenen $\log \beta$ -Werte ein.

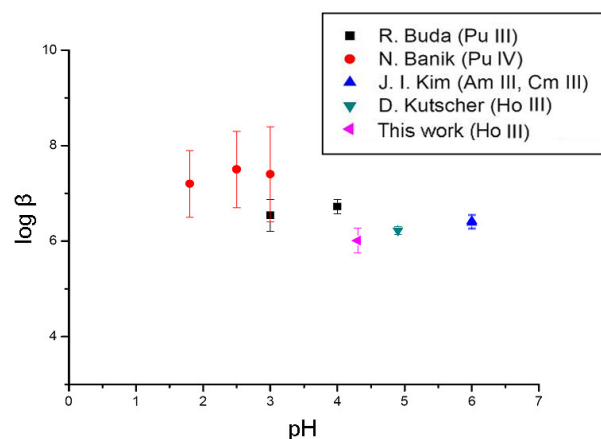


Abbildung 2. Log β -Literaturwerte für die Komplexierung von drei- und vierwertigen Lanthanoiden und Actinoiden durch Aldrich-Huminsäure

Referenzen

- [1] D. Kutscher, Diplomarbeit, Johannes Gutenberg-Universität, Mainz 2007.
- [2] R. Kautenburger, K. Nowotka, H. P. Beck, *Anal. Bioanal. Chem.* **2006**, *384*, 1416-1422.
- [3] K. Nowotka, Dissertation, Universität des Saarlandes, Saarbrücken, 2007.
- [4] J. I. Kim, K. R. Czerwinski, *Radiochim. Acta* **1996**, *73*, 5-10.

Die Arbeit wurde gefördert durch das Graduiertenkolleg GRK 826

Surface enrichment of uranyl oxalate dissolved in room temperature ionic liquids

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Room temperature ionic liquids (RTILs) are salts with a melting point below 100 °C. The cations are usually organic compounds with large side chains to inhibit crystallization. Because of their structural diversity, RTILs exhibit interesting chemical and physical properties, e. g., they are chemical and thermally stable, have a wide electrochemical window, are considered to be inflammable, and have a very low vapour pressure [1]. The latter property allows to investigate RTILs with X-ray photoelectron spectroscopy (XPS). XPS is a surface sensitive analytical method, which provides chemical information of the first few nm of the sample surface. The measurement takes place under ultra-high vacuum, so it is not possible to investigate conventional liquids but RTILs. The XPS spectrometer used in this work (Specs GmbH, Berlin, Germany) employs non-monochromatic $K\alpha$ radiation from a twin anode (Mg/Al) X-ray source XR-50. The XPS spectra were recorded with a constant analyzer pass energy of 50 eV using the hemispherical energy analyzer PHOIBOS 100 MCD.

Two different stock solutions have been prepared. Uranyl oxalate was diluted in 1-butyl-3-methylimidazolium chloride (BmimCl) and 1-butyl-3-methylimidazolium thiocyanate (BmimSCN) (Fig. 1), respectively the uranium concentration of both stock solutions was about 8 mmol/L.

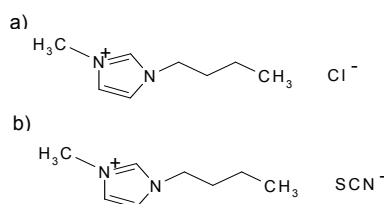


Figure 1: Chemical formula of 1-butyl-3-methylimidazolium chloride (BmimCl) (a) and 1-butyl-3-methylimidazolium thiocyanate (BmimSCN) (b)

The uranium to RTIL ratio in solution was expected to be lower than the detection limit of XPS. But in both cases there is a surface enrichment of uranium. Figure 2 shows XPS spectra of the different stock solutions. In this energy range the N 1s and U 4f lines are visible. Due to the different oxidation states of nitrogen in BmimSCN, its XPS spectrum exhibits two well-resolved N 1s peaks. Using the relative intensities of the XPS lines, it was possible to calcu-

late the atomic ratio between uranium and the RTIL at the surface of the sample.

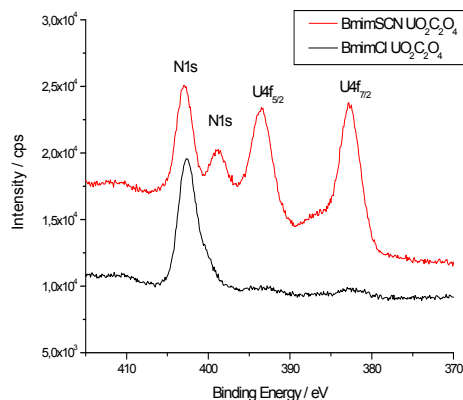


Figure 2: XPS spectra ($E_p = 50$ eV) of uranium oxalate dissolved in 1-butyl-3-methylimidazolium thiocyanate (red) and 1-butyl-3-methylimidazolium chloride (black)

The result is that uranium shows a strong enrichment at the surface, especially in the case of the BmimSCN stock solution. In Table 1 the calculated and the measured U/RTIL ratios are given. The calculated ratio is the amount of uranium, which was expected for a homogenous distribution in the volume. A similar behaviour has been found by Maier [2] concerning platinum coordination compounds in RTILs.

Molecular ratio (U/RTIL)			
BmimCl		BmimSCN	
calculated	measured	calculated	measured
$1.4 \cdot 10^{-3}$	$6.3 \cdot 10^{-3}$	$1.7 \cdot 10^{-3}$	0.2

Table 1: Ratio between uranium and the two RTILs at the surface of the samples

A reason for the lower enrichment of uranium in the BmimCl stock solution might be the higher viscosity that is caused by the different anions of the RTILs.

Reference:

- [1] Binnemans K., Chem., Rev. **107**, 2592-2614 (2007)
 [2] Maier F. et al.; Angew. Chem. Int. Ed. **45**, 7778-7780 (2006)

Multiementalanalyse römischer Ziegel

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In einer Untersuchungsserie von insgesamt sieben römischen Ziegeln wird der Vergleich von Messungen der geochemischen Zusammensetzung antiker keramischer Artefakte mittels INAA, RFA-WD, ICP-OES / ICP-MS unternommen. Die archäologische Untersuchungsabsicht ist dabei die Feststellung der Herstellungsprovenienz. Für die bedeutenden Ziegeleiorte im nördlichen Oberrheingebiet wurden bereits durch kombinierte archäologische, epigraphische und archäometrische Untersuchungen die Charakteristika der Ziegeltonen nach den Gehalten von Oxiden und Spurenelementen der Ziegelprodukte festgestellt. Hierfür wurde geeignetes Referenzmaterial geschaffen und vorgelegt, das für den hier unternommenen Vergleich herangezogen werden kann. Diese Referenzkeramiken erlauben es, künftig auch Fundziegel einzuordnen, die nicht durch archäologische Kriterien, etwa Herstellerstempel, den bekannten Ziegelei-Produktionen zugewiesen werden können. Mit diesem Vorgehen kann ein bedeutendes Forschungsinstrument für archäologische Bauuntersuchungen fortentwickelt werden.

Probenmaterial

Die ausgewählten Materialproben stammen von Ziegeln mit den Fundorten Mainz, Ingelheim und Bad Kreuznach-Planig und weisen militärische Herstellermarken der legio XXII Primigenia und der milites Menapii auf. Es handelt sich um Produkte der in der jeweiligen Zeit (1. – 4. Jahrhundert n. Chr.) zentralen Heeresziegeleien von Rheinabern (Pfalz), Frankfurt a. M.-Nied und Worms. Das Ingelheimer Ziegelstück mit Stempeln Boppard Typ 5 der Flörsheimer Gruppe der legio XXII Primigenia wurde nach den vorliegenden Untersuchungsergebnissen in der Heeresziegelei von Worms hergestellt (Abb. 1). Künftige Untersuchungen zum Beispiel eines umfangreichen Ziegelbefundes in Boppard (Mittelrhein) sollen es ermöglichen, die bestehenden archäologischen Modelle der Beschaffungsmechanismen für öffentliche Baumaßnahmen der Spätantike zu differenzieren.



Abb. 1: Römischer Ziegel mit Stempeln der 22. Legion

Probenaufbereitung und Bestrahlungsprogramm

Bei der INAA wurden die Ziegelsteine in geeignete Bruchstücke zerkleinert und ohne weitere chemische Behandlung am Forschungsreaktor TRIGA Mainz bestrahlt. Für

Kurzzeitbestrahlungen von 1 min wurde ein Rohrpost-System, für Langzeitbestrahlungen von 6 h das Bestrahlungskarussell eingesetzt. Die gammaspektroskopische Analyse erfolgte abgestimmt nach den Halbwertszeiten der Aktivierungsprodukte. Die Probenmenge für Kurzzeitbestrahlungen betrug ca. 15 mg und für Langzeitbestrahlungen 100-150 mg.

Ergebnisse und Diskussion

Die Analysen liefern eine Vielzahl von bis zu 31 Elementen bzw. Spurenelementen (Abb. 2). Hiervon eignen sich für eine Interpretation der Ergebnisse solche Elemente bzw. Elementkombinationen, welche mit einer hohen Genauigkeit und Reproduzierbarkeit gemessen werden können und eine weitgehend homogener Elementverteilung innerhalb eines Ziegels aufweisen wie z.B. Sc, Cr, Fe, Co, Eu, Hf, Sm, Tb und Rb.

Die durch die INAA ermittelten Daten werden mit bisher erhaltenen Konzentrationsangaben aus RFA [1] der gleichen Fundstücke verglichen und zur Analyse römischer Ziegel mittels ICP-OES/-MS [2] in Bezug gesetzt. Von besonderem Interesse ist As, welches mit der RFA nicht nachgewiesen wurde und zukünftig in die Untersuchung der Provenienz einzubeziehen ist.

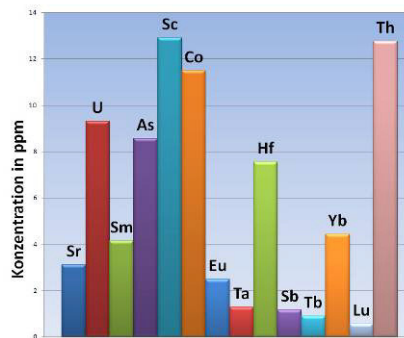


Abb. 2: Elementkonzentrationen römischer Ziegel aus Worms.

Ziel ist es, eine im Hinblick auf die archäologische Fragestellung praktikable Meßroutine für geochemische Provenienzuntersuchungen keramischer Artefakte am Forschungsstandort Mainz zu etablieren.

Referenz

- [1] J. Dolata / H.-J. Mucha / H.-G. Bartel, Archäologische und mathematisch-statistische Neuordnung der Orte römischer Baukeramikherstellung im nördlichen Obergermanien.
- [2] In: Römische Keramik. Xantener Berichte 13 (2003) 381-409. C. Swart, Analyse römischer Ziegel mit ICP-OES / -MS. (Diss. FU Berlin 2005).

Die Datierung und Lokalisierung von Hinterglasmalereien mit Hilfe der Neutronenaktivierungsanalyse

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Seit 1956, als die Neutronenaktivierungsanalyse zum ersten Mal zur Untersuchung kulturgeschichtlicher Objekte eingesetzt wurde [1] hat sich dieses Verfahren als unverzichtbare Methode zur genaueren Bestimmung ihrer regionalen Herkunft und ihres Herstellungsalters erwiesen. Beispielhaft konnte dies an einer Serie von Hinterglasmalereien gezeigt werden, die mit kunsthistorischen Methoden nicht näher klassifiziert werden können.

Hinterglasmalereien wurden im 18. und 19. Jahrhundert in Mitteleuropa in sehr großer Zahl hergestellt, wobei sakrale Motive vorherrschen. Wichtige Zentren der Hinterglasmalerei waren Oberbayern, Schwaben, Ostbayern, Oberösterreich, Böhmen, Schlesien, der Schwarzwald, die Schweiz und Südtirol. Da die Motive ähnlich sind und oft die gleichen Vorlagen verwendet wurden, gelingt es bisher nicht, in den einzelnen Regionen Werkstätten zu definieren oder genauere Hinweise auf die Herstellungszeit zu erhalten. Deshalb sind neue Ansätze zu einer sachgemäßen Dokumentation der Hinterglasmalereien notwendig [2], wozu die Materialanalyse wichtige Informationen liefern kann.

Da in den verschiedenen Regionen unterschiedliche Ausgangsmaterialien verwendet wurden, werkstatttypische Rezepturen zur Glasherstellung zu erwarten waren und Technik der Glasherstellung verbessert wurde, erschien es sinnvoll mit Hilfe der Materialanalyse Proben der Glasscheiben der Hinterglasmalereien zu analysieren, um die Variationsbreite der Zusammensetzungen zu erkennen und regional- bzw. zeittypische Merkmale herauszuarbeiten.

Von 20 Hinterglasbildern, bei denen auf Grund von Darstellungsmerkmalen Herkunft und Datierung ungefähr zu bestimmen war, wurden Proben entnommen und im TRIGA Mark II – Reaktor der Universität Mainz untersucht. Quantitativ bestimmt wurden Ti, V und Mn (Kurzzeitbestrahlung) sowie K, Sc, La, Sm, Ca, Cr, Fe, Co, Zn, Rb, Zr, Sb, Ba, Ce, Eu, Tb, Yb, Lu, Hf und Ta (Langzeitbestrahlung).

Es ergaben sich bei fast allen untersuchten Elementen erhebliche Konzentrationsunterschiede, die in Hinblick auf ihre Aussagekraft zur Bestimmung von Ort und Zeit der Herkunft der Hinterglasbilder interpretiert wurden.

Bei den Hauptbestandteilen fielen vor allem die unterschiedlichen Kaliumgehalte auf, da sehr kalireiche (9 - 17% K) und sehr kaliarme (1 - 4% K) Gläser gefunden wurden. Dieser Unterschied ist auf unterschiedliche Herstellungszeiten zurückzuführen, da im 18. Jahrhundert und im frühen 19. Jahrhundert Pottasche K_2CO_3 als Flussmittel bei der Glasherstellung verwendet wurde, die erst nach 1850, als sich die industrielle Herstellung von Soda Na_2CO_3 nach dem 1863/70 von Solvay entdeckten Verfahren durchsetzte, verdrängt wurde. Somit lassen sich spät hergestellte Bilder von den früh hergestellten Bildern mit Sicherheit trennen.

Die Kalziumgehalte sind gleichmäßig im Bereich zwischen 5 und 13% verteilt. Da in allen untersuchten Regionen unterschiedliche Kalziumwerte angetroffen wurden, ist ein Zusammenhang mit der Herstellungszeit denkbar.

Eisen war ein unerwünschter Bestandteil im Glas, da es für eine grüne Färbung verantwortlich ist. Eisensarme Gläser sind daher besonders qualitativ. Es erstaunt, dass stärker eisenhaltige (0,25 - 0,5 % Fe) Gläser vor allem in Ostbayern und Böhmen vorkommen, wo ein sehr reiner Gangquarz als Rohmaterial zur Verfügung stand, während in Oberbayern die Eisengehalte auf Werte 0,1 - 0,25% Fe absinken, obwohl dort nur ein verunreinigter Quarzsand zur Verfügung stand.

Die Mangangehalte variieren in einem weiten Bereich zwischen 0,005 und 0,4 % Mn. Da wieder in allen Herkunftsgebieten hohe, wie auch niedrigere Mangankonzentrationen vorkommen, ist noch unsicher, ob es sich um eine Verunreinigung durch manganhaltige Mineralien oder um einen bewussten Zusatz von MnO_2 (Braunstein) zur Unterdrückung einer Grünfärbung des Glases durch Eisen handelt.

Bei den Spurenelementen fallen besonders beim Titan und Zirkon beträchtliche Konzentrationsunterschiede auf. Die Titanwerte liegen bei einigen Gläsern unter der Nachweisgrenze, bei anderen erreichen sie Werte von 500 – 850 ppm, wobei Zwischenwerte fehlen. Ähnlich sieht es beim Zirkon aus: entweder liegen die Zirkonwerte unter der Nachweisgrenze oder, wieder ohne Zwischenwerte, bei 12 – 22 ppm. Dies bedeutet, dass als Rohstoff für die Glasherstellung entweder ein sehr reiner magmatisch gebildeter Gangquarz oder ein durch Schwermineralien verunreinigter sedimentärer Sand, in dem Mineralien wie Zirkon ($ZrSiO_4$), Anatas (TiO_2), Rutil (TiO_2) oder Titanit ($CaTiSiO_4$) angereichert sind, verwendet wurde. Hier zeichnen sich deutliche regionale Unterschiede ab, da oberbayerische Gläser zirkon- und titan-reich sind, während diese Elemente in ostbayerischen und böhmischen Gläsern oft nicht mehr nachweisbar sind.

Auch bei den übrigen Spurenelementen sind deutliche Konzentrationsunterschiede zu beobachten.

Statistische Verfahren der Clusteranalyse nutzen diese breiten Schwankungen der Konzentrationsunterschiede und weisen jedem Objekt einen genau definierten Platz in der Gesamtheit der Hinterglasbilder zu, der Zusammengehörigkeiten und somit die Herkunft aus der gleichen Werkstatt erkennen lässt und darüber hinaus in den Herstellungszentren Produkte unterschiedlicher Entstehungszeit sichtbar macht.

References

- [1] J.Riederer: Die Neutronenaktivierungsanalyse in der Archäometrie – eine Bibliographie der frühen Arbeiten von 1956 – 1979, Studien zur Geschichte des Wedenfelder Landes, Serie F Archäometrie, Heft 3, 2007
- [2] J.Riederer: Hinterglasbilder – neue Initiativen zu ihrer Dokumentation. Museum heute, 34, 2008, 61 - 64

Kriminaltechnische Untersuchung von Ziegelsteinen

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Einleitung: Im Rahmen polizeilicher Untersuchungen tritt bisweilen die Frage auf, ob Bruchstücke von Ziegelsteinen, die an einem Tatort aufgefunden werden, mit Steinen in Verbindung stehen, die dem Umfeld eines Tatverdächtigen zuzurechnen sind.

Um derartige Problemstellungen effektiver bearbeiten zu können, wurde das Potential verschiedener elementanalytischer Methoden für die kriminaltechnische Analyse von Ziegelsteinen untersucht.

Analysenmethoden: Für die Bestimmung der Elementkonzentrationen in Ziegelsteinen wurden die Laser Ablation – induktiv gekoppelte Plasma – Massenspektrometrie (LA-ICP-MS), die Röntgenfluoreszenzanalyse (RFA) sowie die instrumentelle Neutronenaktivierungsanalyse (INAA) eingesetzt.

Dabei wurde die Variationsbreite der Elementzusammensetzung innerhalb eines Ziegelsteins, innerhalb einer Gruppe von mehreren Ziegelsteinen aus einer Verpackungseinheit sowie innerhalb einer Gruppe von Ziegelsteinen unterschiedlicher Hersteller untersucht. Entscheidend zu erfahren war, ob in einem einzelnen Stein die Elemente hinreichend homogen verteilt vorliegen und ob sich Steine aus einer Charge ähnlicher sind als Steine aus verschiedenen Produktionschargen.

Probenvorbereitung und Durchführung: Für die Untersuchungen mittels LA-ICP-MS und RFA wurden die Proben mechanisch zerkleinert und mit 87,5 Gew. % Lithiumtetraborat bei einer Gesamteinwaage von 5 g zu Schmelztabletten aufgeschlossen. An diesen Glasmonolithen wurden weitere Untersuchungen durchgeführt (Test auf Homogenität der Schmelztabletten, Bestimmung des Glühverlusts beim Schmelzprozess, Versuchsreihe zum Thema Elementfraktionierung).

Bei der INAA wurden die Ziegelsteine in geeignete Bruchstücke zerkleinert und ohne weitere chemische Behandlung am Forschungsreaktor TRIGA Mainz bestrahlt. Dazu wurden zwei Bestrahlungsprogramme und vier verschiedene Messprogramme gewählt, die auf die unterschiedlichen Halbwertszeiten der Elemente abgestimmt waren.

Ergebnisse: Die mit den drei Untersuchungsmethoden erhaltenen Messergebnisse sind untereinander konsistent und wurden sowohl mit einer konventionellen Methode (Auftragung der Konzentrationen in Säulendiagrammen) als auch mit mathematisch-statistischen Methoden (Multivariate Datenanalyse [1]: Hauptkomponenten- und Clusteranalyse) betrachtet. Aus allen Auswertungsmodellen konnten im Wesentlichen die gleichen Erkenntnisse erzielt werden: die Variation der Elementzusammensetzung ist zwischen Steinen aus verschiedenen Produktionen größer als zwischen Steinen aus einer Charge bzw. innerhalb eines Steins. Damit sind sich die Ziegelsteine

aus der gleichen Produktionsstätte ähnlicher als die Steine aus verschiedenen Produktionen.

Mittels derartiger Untersuchungen von Massenprodukten kann jedoch aufgrund des Fehlens individueller Kennzeichen nicht unmittelbar bewiesen werden, dass zwei Steine aus derselben Quelle stammen. Es werden jedoch Hinweise darauf erlangt, ob eine gemeinsame Herkunft möglich ist oder ausgeschlossen werden kann. Dies muss bei der Befundbewertung berücksichtigt werden.

Zusammenfassung: Für die im Rahmen der kriminaltechnischen Untersuchung von Ziegelsteinen eingesetzten Analysemethoden wurden jeweils geeignete Probenvorbereitungen entwickelt. Alle drei Untersuchungsmethoden lieferten richtige und präzise Konzentrationswerte, was durch Analysen von zertifizierten Standard Referenz Materialien gezeigt werden konnte. Mit allen Methoden konnten ähnliche Erkenntnisse aus den elementanalytischen Daten der Ziegelsteinmessungen gewonnen werden. Somit haben sich die LA-ICP-MS, die RFA und die INAA als Analysemethoden für die kriminaltechnische Untersuchung von Ziegelsteinen bewährt.

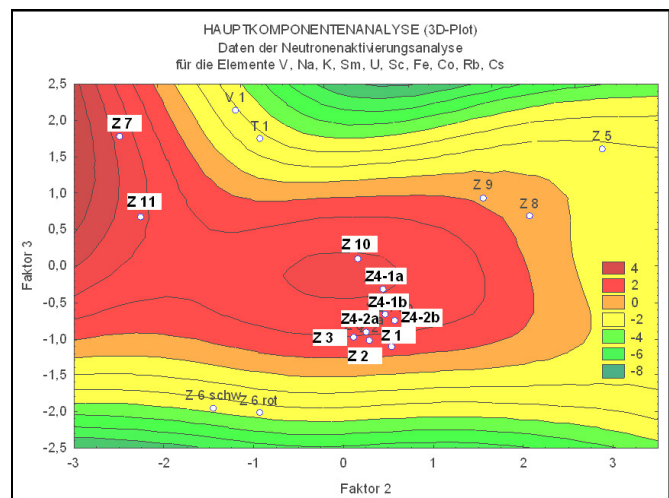


Figure 1. Beispiel für die Hauptkomponentenanalyse mit zehn ermittelten Elementkonzentrationen aus der NAA

Referenzen:

[1] R. Henrion, G. Henrion, Multivariate Datenanalyse, Springer-Verlag, Berlin, 1995

Danksagung

Diese Arbeit wurde finanziell vom Bundeskriminalamt Wiesbaden unterstützt.

Elementanalytische Untersuchungen von Trauben und gärenden Weinen

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Die Konzentrationsentwicklungen der Makroelemente K, Ca und Mg während der Wachstums- und Reifephase von Weintrauben sind bekannt [1]. Angaben zu Konzentrationsentwicklungen hinsichtlich der Spurenelemente fehlen allerdings. Im Hinblick auf die Gärung führen Störungen in deren Ablauf generell zu einer geringeren Qualität des Weines und können viele Ursachen haben. Gärstörungen, deren Ursache auf zu hohe oder zu niedrige Konzentrationen bestimmter Elemente zurückgeführt werden, können durch regelmäßige Analysen erkannt und abgemildert werden.

Daher wurden die Konzentrationsentwicklungen sowohl der Makroelemente K, Mg und Ca als auch der Spurenelemente Na, Al, Mn, Zn, Cu und Rb während der Wachstums- und Reifephase von Weintrauben der Sorten Riesling und Spätburgunder sowie während der Gärung und Reifung der aus diesen Trauben entstandenen Weine an einer Vielzahl von Proben mittels INAA systematisch untersucht. Zusätzlich wurde der Einfluss einer Bentonitschönung und einer Zugabe von Hefenährsalz auf die Elementzusammensetzung des Weines sowie die Abreicherung von Cu mit der Hefe-Starterkultur des Winzers untersucht.

Probennahme, Aufbereitung und Durchführung

Zur Bestimmung der Elementkonzentrationen in den Weintrauben wurden zwischen dem 05.07.07 und 25.09.07 regelmäßig Trauben der Sorten Riesling und Spätburgunder geerntet und manuell gepresst. Während der Gärung wurden in einem Abstand von 2-3 Tagen, nach der Gärung in größeren Abständen, Proben genommen, die Hefe durch Zentrifugation abgetrennt und eingefroren. Vor den Analysen wurden die Flüssigproben durch Zusatz von Salpetersäure und Ethanol chemisch stabilisiert, um das Ausfallen von Weinstein und Trub zu verhindern. Der Hefetrub, der sich am Boden abgesetzt hatte, wurde gefriergetrocknet. Die Proben wurden im Forschungsreaktor TRIGA Mainz bestrahlt, wobei zwei Bestrahlungs- und vier Messprogramme verwendet wurden, die auf die Halbwertszeiten und Konzentrationen der jeweiligen Nuklide abgestimmt waren.

Ergebnisse

Der zeitliche Verlauf verschiedener Elementkonzentrationen wurde ermittelt. Zusätzlich konnten Verdünnungseffekte einiger Elemente (K, Al), bzw. aktiver Transport aus den Beeren (Ca, Mn, Zn) festgestellt werden. Mit zunehmender Beerenreife wird K stark, Na, Al und Rb leicht angereichert. Ca wird stark, Mn und Zn werden leicht abgereichert. Die Konzentrationen von Mg und Cu bleiben im Fehlerbereich konstant. Durch die Beimpfung der Weine mit Starterkulturen werden die Konzentrationen einiger Elemente, wie K, Ca, Mg, Na, Al und Rb leicht, Zn dagegen vergleichsweise stark erhöht. Mn und Cu erfahren dadurch keine Veränderung. Während der Gärung entwickeln sich die Elementkonzentrationen unterschiedlich. Während die Konzentrationen von Na, Mn, Al und Mg beim beimpften Riesling konstant blei-

ben, reichern sich Ca und Rb leicht, K und Cu vergleichsweise stark ab. Die stärkste Veränderung erfährt Zn, was neben der Beimpfung mit einer Hefe-Starterkultur und der Inkorporation durch die Hefe auf die Zugabe von Nährsalz zurückzuführen ist (siehe Abb. 1).

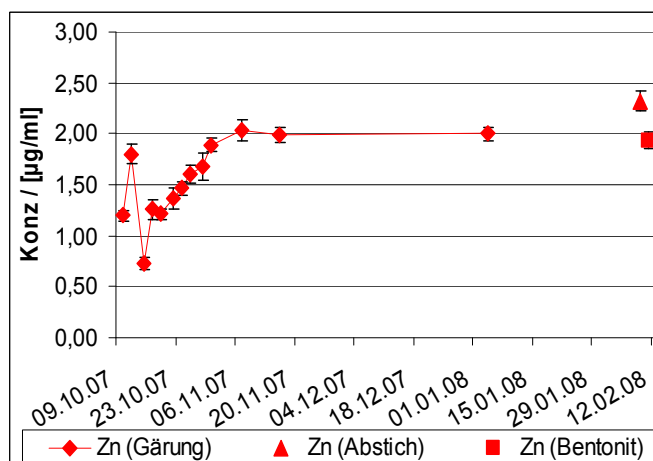


Abb. 1: Konzentrationsverlauf von Zn während der Gärung des mit einer Starterkultur beimpften Rieslings.

Zusammenfassung

Die Entwicklungen der Elementkonzentrationen verlaufen in beiden Traubensorten weitgehend parallel. Durch die verstärkte Wassereinlagerung während der Traubenreife wird bei einigen Elementen ein Verdünnungseffekt sichtbar. Manche Kationen werden dagegen aktiv aus dem Zellsaft transportiert, während die Konzentration anderer Elemente konstant bleibt.

Während der Gärung treten die stärksten Veränderungen hinsichtlich der Elementkonzentrationen auf. Durch die Beimpfung mit Starterkulturen werden zwar die Konzentrationen der meisten Kationen erhöht, diese reichern sich aber im Verlauf der Gärung ab, indem sie entweder von der Hefe inkorporiert oder als schwerlösliche Salze ausgefällt und somit abgetrennt werden. Behandlungen mit Bentonit und Hefenährsalzen beeinflussen die Elementgehalte des Weines – vor allem von Na, Ca und Al (Bentonit) bzw. Zn. Die erzielten Ergebnisse untermauern die Konzentrationsverläufe einiger Spurenelemente während des Gärprozesses in isolierten Laborversuchen von *Azpilicueta et al.* [2]. Diese sind demnach auf die reale Kellerwirtschaft übertragbar.

[1] G. Würdig, R. Woller, *Chemie des Weines*, Eugen Ulmer, 1989, pp 94-100

[2] C. A. Azpilicueta. *Food Research International* 32, 683-689, 1999

Spurenanalyse von gammastrahlenden Radionukliden in der bodennahen Luft

H. Keller, R. Heimann, B. Praast

Seit Beginn des Jahres 1994 werden die aerosol-partikelgetragenen Radionuklide aus der bodennahen Luft mittels einer großvolumigen Sammelapparatur (~100.000 m³/Woche) auf Filtern abgeschieden, die wöchentlich gewechselt werden.

Nach dem Pressen der Filter können die gamma-strahlenden Nuklide ohne weitere Probenvorbereitung direkt gemessen werden.

Nach einer Abklingzeit von etwa einer Stunde wurde zunächst eine Kurzzeitmessung mit einer Messzeit von 10 Stunden durchgeführt, um eventuell vorhandene kurzlebige Radionuklide nachweisen zu können. Aufgrund der hohen Aktivitäten der natürlichen Radionuklide lagen die Erkennungsgrenzen je nach Nuklid bei 0,4 µBq/m³ für Co-57 bis 380 µBq/m³ für Ce-143.

Bei der Langzeitmessung mit einer Messzeit von 60 Stunden wurden nach dem Zerfall der kurzlebigen natürlichen Radionuklide, abhängig von der Gesamtaktivität, die auf dem Filter abgeschieden wurde, folgende Erkennungsgrenzen erreicht:

Cs-137 :	0,1 – 0,6 µBq/m ³
I-131 :	0,3 – 1,6 µBq/m ³
Zr-95 :	0,2 – 1,0 µBq/m ³

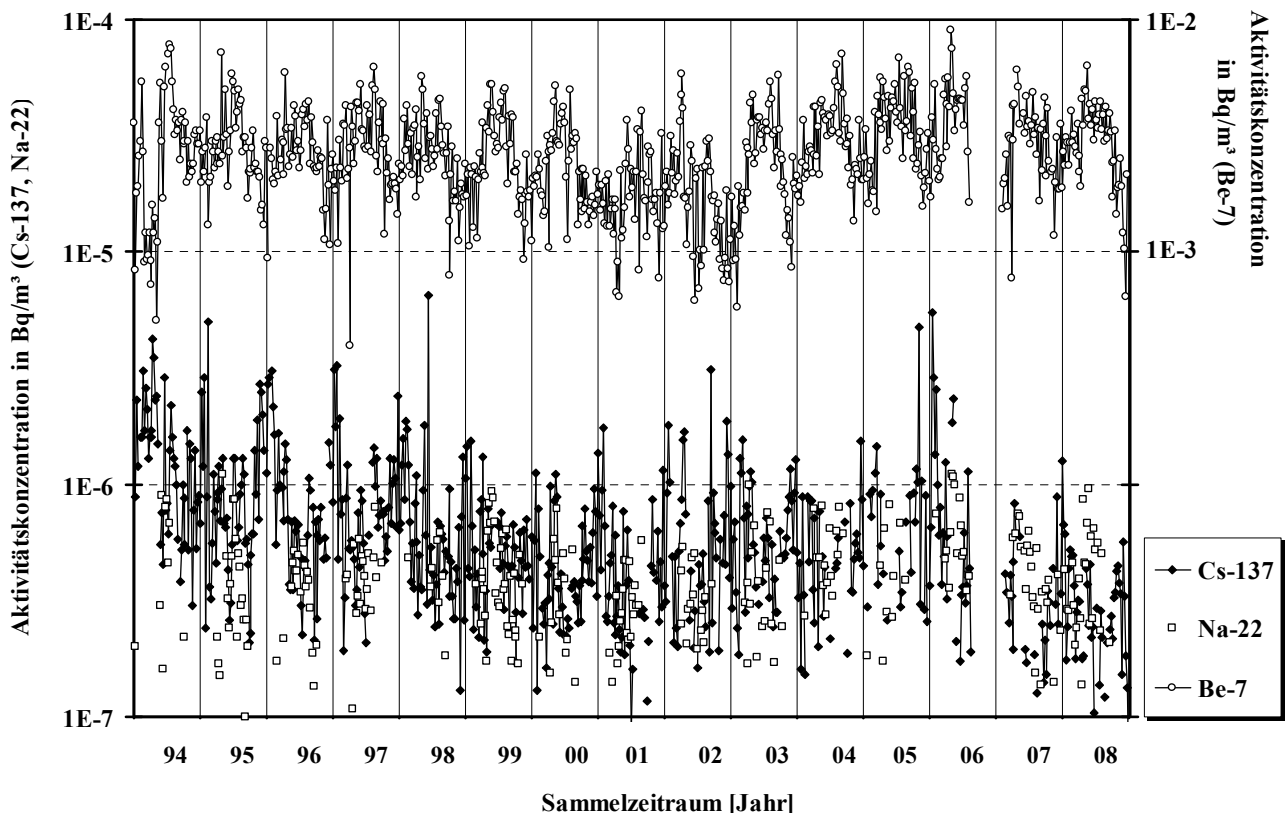
Der Grundpegel der Cs-137-Aktivitätskonzentration war im Vergleich zu den vergangenen Jahren unverändert. Die natürlichen Radionuklide Be-7 und Na-22 werden durch

Kernreaktionen (Spallation) in der Stratosphäre gebildet und gelangen durch Luftmassenaustausch in die bodennahe Luft. Die Werte der Be-7-Aktivitätskonzentrationen liegen wie schon in den vergangenen Jahren bei einigen mBq/m³, die des Na-22 bei maximal 1 µBq/m³ (siehe Abb. 1).

Als mögliche Quellen der Cs-137-Kontamination in der bodennahen Luft kommen Resuspension, großräumiger Transport von Luftmassen aus Gebieten mit höherer Bodenkontamination und Austausch stratosphärischer Luftmassen in Frage [1,2]. Die Beiträge der einzelnen Quellen sind von den örtlichen meteorologischen Gegebenheiten und der Menge der infolge des Reaktorunfalls in Tschernobyl lokal deponierten Aktivität [3] abhängig.

Literatur:

- [1] Hötzl H., Rosner G. und Winkler R.: Sources of Present Chernobyl-derived Caesium Concentrations in Surface Air and Deposition Samples, The Science of the Total Environment 119, 231-242, 1992
- [2] Kulan, A: Seasonal Be-7 and Cs-137 activities in surface air before and after the Chernobyl event, Journal of Environmental Radioactivity 90-2, 140-150, 2006
- [3] Der Bundesminister für Umwelt, Naturschutz und Reaktorsicherheit (Hrsg.): Veröffentlichungen der Strahlenschutzkommission Band 7, Auswirkungen des Reaktorunfalls in Tschernobyl auf die Bundesrepublik Deutschland, 47, Gustav Fischer Verlag, Stuttgart, New York, 1987



D.

Technische Einrichtungen

Technical Facilities

Betrieb des Forschungsreaktors TRIGA Mainz

G. Hampel
Institut für Kernchemie, Universität Mainz

Der Forschungsreaktor TRIGA Mark II wurde im Jahre 2008 schwerpunktmäßig im Dauerbetrieb mit 100 kW Leistung gefahren. Die Betriebsdaten des Reaktors sind in Tabelle 1 zusammengefasst. Gegenüber 2007 ist die Zahl der Betriebstage und der Betriebsstunden leicht erhöht. Insgesamt sind die Schwankungen in der Betriebszeit in den letzten Jahren gering. Die Impulsbestrahlungen haben gegenüber 2007 um etwa 40% abgenommen. Die Ursache hierfür liegt darin, dass das Experiment mit ultrakalten Neutronen am Strahlrohr C verstärkt im Dauerbetrieb durchgeführt wurde. Von den insgesamt 237 Pulsen wurden 92 für Besucher und zu Ausbildungszwecken genutzt. Die freigesetzte Energie und der Spaltstoffverbrauch haben sich auf Grund des längeren Dauerbetriebes im Vergleich zum letzten Jahren erhöht und sind mit den Werten des Jahres 2004 vergleichbar. Seit Inbetriebnahme des TRIGA Mainz im August 1965 sind 176,9 g U-235 abgebrannt worden. Änderungen in der Kernbeladung erfolgten in 2008 nicht, d.h. der Kern des Mainzer Reaktors ist seit Februar 2007 mit 76 Brennelementen beladen.

In Tabelle 2 ist die Zahl der Bestrahlungen in den verschiedenen Bestrahlungspositionen aufgeführt. Am häufigsten wurde das Bestrahlungskarussell genutzt mit einer im Vergleich zum Vorjahr um etwa 100 erhöhten Anzahl von Bestrahlungen. Dieses ist auf eine Vielzahl von Neutronenaktivierungsanalysen insbesondere für archeometrische Untersuchungen zurückzuführen. Der größere Bedarf an der Neutronenaktivierungsanalyse spiegelt sich auch in einer im Vergleich zum Vorjahr höheren Anzahl an Rohrpostbestrahlungen wieder. Das Zentrale Bestrahlungsrohr wurden in 2008 verstärkt für den Nachweis von Fe in Silizium in der Solarzellenforschung eingesetzt, so dass hier die Anzahl der Proben stieg.

Am Strahlrohr A wurden Experimente zur Untersuchung der chemischen Eigenschaften der schwersten Elemente durchgeführt und erstmals ein Gasjet-System mit Kohlenstoffaerosolen betrieben. Am Strahlrohr B befindet sich in Zusammenarbeit mit dem MPI für Kernphysik in Heidelberg und der Helmholtz-Nachwuchsgruppe im Institut für Kernchemie eine Anlage im Aufbau, bei der mittels Massenspektrometrie und Laserspektroskopie die Eigenschaften neutronenreicher Radionuklide mit höchster Präzision ermittelt werden sollen.

Am Strahlrohr C ist in Kooperation mit dem Institut für Physik der Universität Mainz und der TU München eine Apparatur zur Erzeugung von ultrakalten Neutronen (UCN) aufgebaut, die für verschiedene Experimente betrieben wurde. Die UCN-Quelle wurde im Vergleich zu 2007 nicht nur im Pulsbetrieb, sondern verstärkt im Dauerbetrieb eingesetzt. Am Strahlrohr D befindet sich eine neue und im Vergleich zur Strahlrohr C leistungsstärkere Quelle im Aufbau.

Die Thermische Säule wurde in 2008 im Rahmen des Projektes zur Behandlungen von Lebermetastasen mittels Bor-Neutronen-Einfang-Therapie verstärkt zur Bestrahlung von borhaltigen Gewebeschnitten eingesetzt, mit dem Ziel, radiographisch die Borkonzentration in den Proben zu bestimmen. Zusätzlich wurden Bestrahlungen zur Dosisermittlung für das Organ durchgeführt.

Die Gesamtzahl der Bestrahlungen ist in 2008 annähernd konstant geblieben. Wie in den Vorjahren wurden weit mehr als 3000 Bestrahlungen durchgeführt. Das Spektrum der Reaktornutzer (Tabelle 3) ist bei den externen Bestrahler kaum verändert.

Im Jahre 2008 besichtigten 660 Personen den Reaktor (Tabelle 4), wobei etwa 75 Stunden für Führungen und Erläuterungen der Forschungsarbeiten am hiesigen Institut aufgewandt wurden.

Tabelle 1: Betriebsdaten des Reaktors

Betriebsdaten	von 1965 bis 2002	2003	2004	2005	2006	2007	2008	insgesamt
Betriebstage	7180	192	188	202	205	191	202	8360
Betriebsstunden	36364	850	918	898	944	924	970	41868
Impulse	14726	94	112	266	746	593	237	16774
davon Reaktivität bis 1,25 \$	333	2	4	17	6	26	13	401
1,50 \$	11583	83	82	228	673	446	157	13252
1,75 \$	233	3	4	13	6	8	6	273
2,00 \$	2577	6	22	8	61	113	61	2787
Freigesetzte Energie (MWh)	2869,1	76,4	82,2	77,5	66,9	74,2	83,4	3329,7
davon im Dauerbetrieb	2869,1	76,2	82	77,1	65,7	73,1	82,9	3326,1
im Impulsbetrieb	34,7	0,1	0,2	0,2	0,4	1,2	1,1	38
Spaltstoffverbrauch [g U-235]	145,1	4,2	3,9	4,3	4	3,5	3,9	172,5

Tabelle 2: Zahl der Bestrahlungen in den verschiedenen Bestrahlungspositionen des Reaktors

Bestrahlungsposition	von 1965 bis 2002	2003	2004	2005	2006	2007	2008	insgesamt
Bestrahlungskarussell	53024	1946	1505	1618	1460	1947	2044	63544
Rohrpost 1, 2 und 3	62786	81	22	241	364	520	597	64611
Schnelle Rohrpostanlagen	135064	110	61	--	--	--	--	135235
Strahlrohre	10040	115	121	747	1139	853	293	13308
Zentrales Bestrahlungsrohr	2628	55	61	71	53	83	119	3070
Reaktortank (auf dem Kern)	1240	--	--	--	--	--	--	1240
Thermische Säule	563	--	0	63	53	69	171	919
alle Bestrahlungspositionen	265345	2307	1770	2740	3069	3472	3224	281927

Tabelle 3: Benutzer des Reaktors im Jahre 2008**Universität Mainz****Zahl der Bestrahlungen**

Institut für Kernchemie

1783

Externe Bestrahler**Zahl der Bestrahlungen**

BASF Ludwigshafen

2

Bergakademie Freiberg

1211

Gesellschaft für Schwerionenforschung Darmstadt

5

Forschungszentrum Karlsruhe, Inst. für Interdisz. Isotopenforschung

8

AREVA NP GmbH Karlstein

194

Arotop food & environment GmbH

4

Universität Köln

10

Universität Marburg

7

insgesamt: 3224**Vorjahr: 3552****Tabelle 4: Besucher des Reaktors im Jahre 2008**

Datum	Besucher / Anlass	Anzahl
15.01.2008	Rentnerverein Hochheim	10
07.02.2008	Tag der offenen Tür	73
07.03.2008	Kernchemisches Praktikum	15
11.03.2008	Strahlenschutz-Kurs für Lehrkräfte	39
12.03.2008	Strahlenschutz-Kurs für Lehrkräfte	42
08.04.2008	Berufsbildende Schule BBS-Technik I	14
09.04.2008	Diltheyschule Wiesbaden	9
10.04.2008	Kurs Strahlenschutz für Biologen	79
07.05.2008	Feuerweht-Kurs	17
19.05.2008	Studenten aus South Carolina, USA	8
02.06.2008	Universidad Nacional do Colombia	19
10.06.2008	Uni Marburg	21
11.06.2008	Campus Grün	10
19.06.2008	Lions Club Oppenheim	26
25.06.2008	Ferienakademie Schülerlabor	15
22.08.2008	Kernchemisches Praktikum	18
22.08.2008	SEACAVA	11
04.09.2008	Strahlenschutzkurs	12
09.09.2008	Rabanus-Maurus-Gymnasium	8
11.09.2008	FH Wiesbaden	12
18.09.2008	Jahrestagung des Fachverbandes für Strahlenschutz	10
17.10.2008	Kernchemisches Praktikum	18
20.10.2008	Gutenberg - Akademie	13
22.10.2008	Forum der Jungchemiker	26
23.10.2008	Gutenbergschule Wiesbaden	13
23.10.2008	IGS Ingelheim	18
10.11.2008	Mathias Grünwald Gymnasium	40
21.11.2008	Betriebsarzt	13
01.12.2008	Max-Planck-Gymnasium Saarlouis	41
09.12.2008	Uni-Klinikum Mainz / Praktikanten	10
	insgesamt	660

Personendosisüberwachung

I. Onasch, B. Praast

Ergebnisse der amtlichen Personendosisüberwachung in den Jahren 1999 bis 2008 (Jahresdosen in mSv). Die untere Nachweisgrenze der Personendosis bei monatlicher Auswertung beträgt 0,1 mSv.

	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008
	Anzahl der ausgewerteten Dosimeter									
	957	866	954	934	862	903	961	993	1006	1146
Jahresdosen in mSv	Anzahl der Personen									
5,0 - 6,0	-	-	-	-		-	-	-	-	1
4,0 - 5,0	-	-	-	-	1	-	-	-	-	-
3,0 - 4,0	2	2	2	-	1	-	-	-	-	-
2,0 - 3,0	1	-	-	1	-	1	2	2	2	3
1,0 - 2,0	2	1	-	1	2	3	-	-	2	3
0,5 - 1,0	-	1	-	2	3	1	1	2	3	5
0,1 - 0,5	6	6	4	7	9	17	25	8	26	14

Von im Mittel 96 überwachten Personen im Jahr 2008 erhielten 70 Personen Jahresdosen, die sämtlich unterhalb der Nachweisgrenze (< 0,1 mSv / Monat) lagen.

Abgabe radioaktiver Stoffe

A. Heiser, B. Praast, H. Keller

Über die Abluft wurden im Berichtsjahr 180 GBq Edelgase abgegeben (Tab.1). Dabei handelte es sich ausschließlich um das durch Neutronenaktivierung des in der Luft enthaltenen Argons gebildete kurzlebige Isotop Ar-41 ($t_{1/2} = 1,83$ h). Dies entspricht 36 % des genehmigten Wertes. Die aerosolpartikelgebundene Aktivität lag unterhalb der geforderten Nachweisgrenzen. Das Abluftvolumen betrug $6,9 \text{ E}+07 \text{ m}^3$.

	genehmigt	abgegeben
Edelgase	500 GBq	180 GBq
Aerosole	0,5 GBq	< NWG

Tabelle 1: Mit der Abluft im Jahr 2008 abgeleitete Aktivität

Im Berichtsjahr wurden keine radioaktiven Stoffe als Abfälle abgegeben.

Mit dem Abwasser wurden im Berichtsjahr folgende radioaktiven Stoffe abgegeben:

Nuklid	Aktivität in Bq	Nuklid	Aktivität in Bq
H-3	2,5E+05	U-235	4,4E+02
Co-60	6,8E+04	U-238	2,2E+04
Se-75	6,4E+04	Np-237	1,0E+05
Cs-134	8,3E+03	Pu-238	1,9E+05
Cs-137	8,5E+05	Pu-239/240	1,7E+05
Th-227	4,0E+02	Am-241	6,8E+03
Th-228	7,9E+03	Cm-246	8,5E+03
Th-230	1,8E+03	Cm-248	4,0E+03
Th-232	5,4E+02	Cf-249	9,1E+03
U-234	1,4E+04	Cf-251	4,7E+03

Tabelle 2: Mit dem Abwasser im Jahr 2008 abgegebene radioaktive Stoffe

E.

**Veröffentlichungen, Vorträge
Lehrveranstaltungen**

**Publications, Conference Contributions
Teaching Activities**

Diplomarbeiten und Dissertationen

Diplom

Beyerlein, Friederike

Synthese und nukleophile ^{18}F -Markierung von Tyrosin-Derivaten und automatischen Modellverbindungen

Even, Julia

Unterpotentialabscheidung Ruthenium und Osmium

Feige, Markus

Untersuchungen zum zeitlichen Verlauf der Elementkonzentrationen während der Traubenreife und der Mostfermentation mittels Neutronenaktivierungsanlage

Fröhlich, Daniel

Untersuchung der Sorption von Np(V) an Opalinuston

Gromm, Enrico

CE-AD-ICP-MS-Kopplung zur Bestimmung der Komplexbildungs-Konstanten für die Komplexierung von Lanthanoiden mit Huminsäure

Hampel, Jonathan

Neutronenaktivierungsanalyse an Silicium und Siliciumcarbid

Hild, Daniel

Flüssig-Flüssig-Extraktion mit dem MikroSISAK-System

Kramer, Vasko

Synthese, ^{18}F -Markierung und Evaluierung von MDL 100907-Derivaten zur Visualisierung von Veränderungen der endogenen Serotinkonzentration mittels der Positronen-Emissions-Tomographie

Krieger, Andreas

Aufbau eines jodstabilisierten Farbstofflasers zur kollinearen Spektroskopie und sein Einsatz zur Hochspannungsmessung an ISOLDE

Scheid, Nicole

Kriminaltechnische Untersuchung von Ziegelsteinen

Schütz, Christian

Borbestimmung in Gewebeproben im Rahmen der Entwicklung eines Behandlungsprotokolls für die Bor-Neutronen-Einfangtherapie an einer autotransplantierten Leber

Zoller, Frederic

Radiosynthese und Evaluierung von ^{68}Ga -markierten Porphyrin-Derivaten für die Positronen-Emissions Tomographie

Dissertationen

Reich, Tatiana

New regularization method for EXAFS analysis-Application to uranium and plutonium sorption onto Kaolinite

Riß, Patrick

On the development of novel cocaine analogues for in vivo imaging of the dopamine transporter status

Vilas, Victor-Vincente

Study of the interactions of Neptunium with humic substances and the clay mineral Montmorillonite by direct and non-direct speciation methods

Veröffentlichungen und Vorträge der Mitarbeiter der berichtserstattenden Arbeitsgruppen

Veröffentlichungen

- I. Altarev, F. Atchison, M. Daum, A. Frei, E. Gutmiedl, G. Hampel, F.J. Hartmann, W. Heil, A. Knecht, J.V. Kratz, T. Lauer, M. Meier, S. Paul, Y. Sobolev, N. Wiehl
Direct Experimental Verification of Neutron Acceleration by the Material Optical Potential of Solid $^2\text{H}_2$
Phys. Rev. Lett. 100, 014801 (2008)
- I. Altarev, M. Daum, A. Frei, E. Gutmiedl, G. Hampel, F.J. Hartmann, W. Heil, A. Knecht, J.V. Kratz, T. Lauer, M. Meier, S. Paul, U. Schmidt, Y. Sobolev, N. Wiehl and G. Zsigmond
Neutron velocity distribution from a superthermal solid $^2\text{H}_2$ ultracold neutron source
Eur. Phys. J. A. 37, 9 (2008)
- S. Amayri, N.L. Banik, M. Breckheimer, R.A. Buda, S. Bürger, J. Drebert, A. Jermolaev, J.V. Kratz, B. Kuczewski, D. Kutscher, T.Ye. Reich, T. Reich, N. Trautmann
Interaction of neptunium and plutonium with humic substances and kaolinite
Forschungszentrum Karlsruhe, Wiss. Berichte FZKA 7407, 141 (2008)
- M. Astia, G. De Pietria, A. Fraternalia, E. Grassib, R. Sghedonib, F. Fioronib, F. Rösch, A. Versaria, D. Salvoa
Validation of $^{68}\text{Ge}/^{68}\text{Ga}$ generator processing by chemical purification for routine clinical application of ^{68}Ga -DOTATOC.
Nuclear Medicine Biology 35, 721 (2008)
- F. Becher, S. Nagels, B. Burgkhardt, R. Böttger, A. L. Aguilar, G. Hampel, B. Wortmann
Dosimetry in mixed gamma-neutron radiation fields and energy compensation filters for CaF_2 : Tm TL detectors, Radiation Measurements 43, 921 (2008)
- T. Betzel, T. Heß, B. Waser, J.-C. Reubi, F. Rösch
closo-borane conjugated regulatory peptides retain high biological affinity: Synthesis of *closo*-borane conjugated Tyr³-octreotate derivatives for BNCT.
Bioconjug. Chem. 19(9), 1796 (2008)
- R.A. Buda, N.L. Banik, J.V. Kratz, N. Trautmann
Studies of the Ternary Systems Humic Substances – Kaolinite – Pu(III) and Pu(IV)
Radiochim. Acta 96, 657 (2008)
- S. Dierking, S. Amayri, T. Reich
Actinide sorption studies using the isotopes ^{237}Np and ^{239}Np
J. Nuc. Sci. Technol., S5, 1 (2008)
- G. W. F. Drake, Z.-T. Lu, W. Nörtershäuser, Z.-C. Yan
Halo Nuclei in Laser Light Lecture Notes in Physics 745, Precision Physics of Simple Atoms and Molecules, 131-153, Springer (2008)
- J. Dvorak, W. Bröchle, M. Chelnokov, Ch. E. Düllmann, Z. Dvorakova, K. Eberhardt, E. Jäger, R. Krücken, A. Kuznetsov, Y. Nagame, F. Nebel, K. Nishio, R. Perego, Z. Qin, M. Schädel, B. Schausten, E. Schimpf, R. Schuber, A. Semchenkov, P. Thörle, A. Türler, M. Wegrzecki, B. Wierczinski, A. Yakushev, A. Yeremin
Observation of $3n$ evaporation channel in the complete hot-fusion reaction $^{26}\text{Mg} + ^{248}\text{Cm}$ leading to the new superheavy nuclide ^{271}Hs
Phys. Rev. Lett., 100, 132503 (2008)
- K. Eberhardt, W. Bröchle, Ch. E. Düllmann, K.E. Gregorich, W. Hartmann, A. Hübner, E. Jäger, B. Kindler, J.V. Kratz, D. Liebe, B. Lommel, H.-J. Maier, M. Schädel, B. Schausten, E. Schimpf, A. Semchenkov, J. Steiner, J. Szerypo, P. Thörle, A. Türler, A. Yakushev
Preparation of targets for the gas-filled recoil separator TASCA by electrochemical deposition and design of the TASCA target wheel assembly
Nucl. Instr. Meth. Phys. Res. A590, 134 (2008)
- N. Erdmann, G. Passler, N. Trautmann, K. Wendt
Resonance Ionization Mass Spectrometry for Trace Analysis of Long-lived Radionuclides
in: Analysis of Environmental Radionuclides, Volume 11 (P.P. Povinec, ed.), Elsevier, Amsterdam, 2008, 331-354

- C. Fehr, I. Yakushev, N. Hohmann, H.-G. Buchholz, C. Landvogt, H. Deckers, A. Eberhardt, M. Kläger, M.N. Smolka, A. Scheurich, T. Dielentheis, L.G. Schmidt, F. Rösch, P. Bartenstein, G. Gründer, M. Schreckenberger
Association of low striatal dopamine D2 receptor availability with nicotine dependence similar to that seen with other drugs of abuse.
Am. J. Psychiatry 165, 507 (2008)
- G. Gambarini, F. Gallivanone, A. Carrara, S. Nagels, L. Vogtländer, G. Hampel, L. Pirola, Study of reliability of TLDs for the photon dose mapping in reactor neutron fields for BNCT
Radiation Measurements 43, 1118 (2008)
- G. Geipel, S. Amayri, G. Bernhard
Mixed complexes of alkaline earth uranyl carbonates: A laser-induced time-resolved fluorescence spectroscopic study
Spectrochim. Acta, A71, 53 (2008)
- G. Gründer, C. Fellows, H. Janouschek, T. Veselinovic, C. Boy, A. Bröcheler, K.M. Kirschbaum, S. Hellmann, K.M. Spreckelmeyer, C. Hiemke, F. Rösch, W.M. Schaefer, I. Vernaleken
Brain and plasma pharmacokinetics of aripiprazole in patients with Schizophrenia: An [¹⁸F]Fallypride PET study.
Am. J. Psychiatry 165, 988 (2008)
- G. Hampel, K. Eberhardt, S. Zauner
Ausbildung und Kompetenzerhalt in Kernchemie, Kernphysik und Strahlenschutz am Forschungsreaktor TRIGA Mainz, Kompetenz im Strahlenschutz – Ausbildung, Weiterbildung und Lehre- Tagungsband - ISBN:978-3-8249-1193-6
- J. Hampel, A. Banerjee, T. Häger, G. Hampel, I. Conejos Sánchez, S. Zauner
Neutron Activation Analysis for the Determination of Elements in Ivory
BfN-Skripten 228, Bundesamt für Naturschutz, Bonn-Bad Godesberg 2008, 87
- M.M. Herth, F. Debus, M. Piel, M. Palner, G.M. Knudsen, H. Lüddens, F. Rösch
Total synthesis and evaluation of [¹⁸F]MHMZ.
Bioorg. Med. Chem. Lett. 18(4), 1515 (2008)
- H. Hummrich, N.L. Banik, M. Breckheimer, W. Bröchle, R. Buda, F. Feist, E. Jäger, J.V. Kratz, B. Kuczewski, D. Liebe, L. Niewisch, M. Schädel, B. Schausten, E. Schimpf, and N. Wiehl
Electrodeposition methods in superheavy element chemistry
Radiochim. Acta 96, 73 (2008)
- Y. Ishii, A. Toyoshima, K. Tsukada, M. Asai, H. Toume, I. Nishinaka, Y. Nagame, S. Miyashita, T. Mori, H. Suganuma, H. Haba, M. Sakamaki, S. Goto, H. Kudo, K. Akiyama, Y. Oura, H. Nakahara, Y. Tashiro, A. Shinohara, M. Schädel, W. Bröchle, V. Pershina, and J.V. Kratz
Fluoride complex formation of element 104, Rutherfordium (Rf) investigated by cation-exchange chromatography
Chem. Lett. 37, 288 (2008)
- M. Jennewein, M.A. Lewis, D. Zhao, E. Tsyganov, N. Slavine, J. He, L. Watkins, P.P. Antich, A. Hermanne, F. Rösch, R.P. Mason, P.E Thorpe
Vascular imaging of solid tumors in rats with a radioactive arsenic-labeled antibody that binds exposed phosphatidylserine.
Clin. Cancer Res. 14/5, 1377 (2008)
- J. Ketelaer, J. Krämer, D. Beck, K. Blaum, M. Block, K. Eberhardt, G. Eitel, R. Ferrer, C. Geppert, S. George, F. Herfurth, J. Ketter, Sz. Nagy, D. Neidherr, R. Neugart, W. Nörtershäuser, J. Repp, C. Smorra, N. Trautmann, C. Weber
TRIGA-SPEC: A Setup for Mass Spectrometry and Laser Spectroscopy at the Research Reactor TRIGA Mainz
Nucl. Instr. Meth. Phys. Res. A594, 162 (2008)
- T. Kienast, T. Siessmeier, J. Wrase, D.F. Braus, M.N. Smolka, H.G. Buchholz, M. Rapp, M. Schreckenberger, F. Rösch, P. Cumming, G. Gründer, K. Mann, P. Bartenstein, A. Heinz
Ratio of dopamine synthesis capacity to D2 receptor availability in ventral striatum correlates with central processing of affective stimuli.
Eur. J. Nucl. Med. Mol. Imaging 35, 1147 (2008)
- H.-J. Kluge, F. Herfurth, O. Kester, W. Nörtershäuser, and W. Quint
How to measure nuclear ground-state properties in simple systems such as ¹¹Li or U⁹¹⁺?
Nucl. Instr. Meth. Phys. Res. B 266, 4542 (2008)

- H.-J. Kluge, T. Beier, K. Blaum, L. Dahl, S. Eliseev, F. Herfurth, B. Hofmann, O. Kester, S. Koszudowski, C. Kozuharov, G. Maero, W. Nörtershäuser, J. Pfister, W. Quint, U. Ratzinger, A. Schempp, R. Schuch, T. Stöhlker, R.C. Thompson, M. Vogel, G. Vorobjev, D.F.A. Winters, G. Werth
HITRAP: A facility at GSI for Highly Charged Ions
Adv. Quantum Chem. 53, 83 (2008)
- A. Krepelová, T. Reich, S. Sachs, J. Drebert, G. Bernhard
Structural characterization of U(VI) surface complexes on kaolinite in the presence of humic acid using EXAFS spectroscopy
J. Colloid Interface Sci. 319, 40 (2008)
- D. Liebe, K. Eberhardt, W. Hartmann, T. Häger, A. Hübner, J.V. Kratz, B. Kindler, B. Lommel, P. Thörle, M. Schädel, J. Steiner
The application of neutron activation analysis, scanning electron microscope, and radiographic imaging for the characterization of electrochemically deposited layers of lanthanide and actinide elements
Nucl. Instr. Meth. Phys. Res. A590, 145 (2008)
- B. Lommel, W. Bröchle, K. Eberhardt, W. Hartmann, A. Hübner, B. Kindler, J.V. Kratz, D. Liebe, M. Schädel, J. Steiner
Backings and Targets for Chemical and Nuclear Studies of Transactinides with TASCA
Nucl. Instr. Meth. Phys. Res. A590, 141 (2008)
- C. Novotny, G. Ewald, C. Geppert, G. Huber, S. Karpuk, W. Nörtershäuser, G. Saathoff, S. Reinhardt, A. Wolf, D. Schwalm, G. Gwinner, T. Kühl, M. Steck, T.W. Hänsch, R. Holzwarth, T. Udem, B. Bernhardt
Experimental Test of Special Relativity by Laser Spectroscopy
submitted to Phys. Rev. Lett.
- C. Novotny, B. Bernhardt, D. Bing, G. Ewald, C. Geppert, G. Gwinner, G. Huber, S. Karpuk, H.-J. Kluge, T. Kühl, W. Nörtershäuser, S. Reinhardt, G. Saathoff, D. Schwalm, T. Stöhlker, and A. Wolf
Towards a precision test of time dilation at high velocity
Canad. J. Phys., in print
- Z. Qin, W. Bröchle, D. Ackermann, K. Eberhardt, F.P. Heßberger, E. Jäger, J.V. Kratz, P. Kuusiniemi, D. Liebe, G. Münzenberg, D. Nayak, Yu.N. Novikov, M. Schädel, B. Schausten, E. Schimpf, A. Semchenkov, B. Sulignano, P. Thörle and X.L. Wu
Search for the “missing” α -decay branch in ^{239}Cm
Radiochim. Acta 96, 455 (2008)
- P.J. Riss, F. Rösch
A convenient chemo-enzymatic of *trans*-1-toluenesulfonyloxymethyl-2-fluoromethyl-cyclopropane
Org. Biomol. Chem. 6, 4567 (2008)
- P.J. Riss, C. Kroll, V. Nagel, F. Rösch
NODAPA-OH and NODAPA-(NCS)n: Synthesis, ^{68}Ga -radiolabelling and in vitro characterisation of novel versatile bifunctional chelators for molecular imaging
Bioorg. & Medicinal Chem. Letters 18, 5364 (2008)
- F. Rösch
Radiochemistry and Radiopharmaceutical Chemistry for Medicine
In: Encyclopedia of Life Support Systems, Eolss Publishers Co Ltd, Oxford, UK, 2008
- R. Sanchez, M. Záková, C. Geppert, J. Krämer, M. Nothhelfer, D. Tiedemann, W. Nörtershäuser
Frequency-Comb based Laser Spectroscopy for Nuclear Structure
Canad. J. Phys., in print
- N. Scheid, G. Hampel, J.V. Kratz, P. Weiss, S. Menges M. Dücking, S. Becker
Forensic investigation of brick stones and application of multivariate statistical methods on elemental analysis data
ENFSI EWG Paint Glass newsletter 2008
- A. Toyoshima, H. Haba, K. Tsukada, M. Asai, K. Akiyama, S. Goto, Y. Ishii, I. Nishinaka, T.K. Sato, Y. Nagame, W. Sato, Y. Tami, H. Hasegawa, K. Matsuo, D. Saika, Y. Kitamoto, A. Shinohara, M. Ito, J. Saito, H. Kudo, A. Yokoyama, M. Sakama, K. Sueki, Y. Oura, H. Nakahara, M. Schädel, W. Bröchle, J.V. Kratz
Formation of hexafluoro complex of Rutherfordium in mixed HF/HNO₃ solutions
Radiochim. Acta 96, 125 (2008)

I. Vernaleken, C. Fellows, H. Janouschek, A. Bröcheler, T. Veselinovic, C. Landvogt, C. Boy, H.G. Buchholz, K. Spreckelmeyer, P. Bartenstein, P. Cumming, C. Hiemke, F. Rösch, W. Schäfer, D.F. Wong, G. Gründer
Striatal and extrastriatal D2/D3-receptor-binding properties of ziprasidone: a positron emission tomography study with [¹⁸F]Fallypride and [¹¹C]raclopride (D2/D3-receptor occupancy of ziprasidone).
J. Clin. Psychopharmacol. 28(6), 608 (2008)

I. Vernaleken, C. Fellows, H. Janouschek, A. Bröcheler, T. Veselinovic, C. Landvogt, C. Boy, H.-G. Buchholz, P. Bartenstein, P. Cumming, C. Hiemke, F. Rösch, W. Schäfer, D.F. Wong, G. Gründer
Striatal and extrastriatal D_{2/3} receptor binding properties of ziprasidone: a PET study with [¹⁸F]Fallypride.
J. Neuropsychopharmacology 2008, accepted

V. Vicente Vilas, S. Rubert de la Rosa, J.V. Kratz
Sorption of Np(V) onto Hybrid Clay-Based Materials: Montmorillonite-Melanoidin
Proc. 14th Meeting of the International Humic Substances Society (IHSS), Moscow - St. Petersburg, Vol. 2, 587-590 (2008)

Z. C. Yan, W. Nörtershäuser, and G. W. F. Drake
High Precision Atomic Theory for Li and Be⁺: QED Shifts and Isotope Shifts
Phys. Rev. Lett. 100, 243002 (2008)

Koll 47: R3B-Kollaboration

PRZEMYSLAW ADRIK¹³, FAROUK AKSOUH¹⁰, ALEJANDRO ALGORA⁴, JIM AL-KHALILI⁴⁹, GEORGI ALKHAZOV³⁰, HECTOR ALVAREZ-POL⁴⁷, IRINA ANGELESCU¹⁸, THOMAS AUMANN¹³, VLADIMIR AVDEICHIKOV²⁸, CHARLES BARTON⁵⁰, JOSE BENLIURE⁴⁷, CARLOS BERTULANI³⁵, SUDEB BHATTACHARYA³³, MICHAEL BÖHMER³⁹, DAVID BOILLEY¹², KONSTANZE BORETZKY¹³, MARIA JOSÉ BORGE⁹, ALEXANDRE BOTVINA¹⁶, ALAIN BOUDARD¹⁰, FRANCISCO CALVINO⁵¹, ENRIQUE CASAREJOS⁴⁷, WILTON CATFORD⁴⁹, BO CEDERWALL²⁶, ROBERT CHAPMAN⁴⁶, MARIELE CHARTIER⁴⁴, AUDREY CHATILLON¹³, MADALINILIE CHERCIU¹⁸, LEONID CHULKOV³², PATRICK COLEMAN-SMITH⁷, DOLORES CORTINA-GIL⁴⁷, MARGIT OSATLOS⁴, DAVID CULLEN⁴⁵, BORIS DANILIN³², USHASI DATTA PRAMANIK³³, JEAN-ERIC DUCRET¹⁰, IGNACIO DURAN⁴⁷, PETER EGELHOF¹³, MICHAEL ELVERS⁴², HANS EMLING¹³, JOACHIM ENDERS³⁸, VLADIMIR EREMIN¹⁹, SERGEY N. ERSHOV²³, SAMUEL ESPAÑA⁴⁰, THOMAS FAESTERMANN³⁹, DIMITRI FEDOROV⁴, HANS FELDMER¹³, BEATRIZ FERNANDEZ DOMINGUEZ⁴⁴, ANDREY S. FORMICHEV²³, CHRISTIAN FORSSÉN²⁷, LUIS M. FRAILE⁴⁰, SEAN FREEMAN⁴⁵, MARTIN FREER⁶, JÜRGEN FRIESE³⁹, HANS FYNBO¹, ZOLTAN GACSI⁴, DANIEL GALAVIZ⁹, EDUARDO GARRIDO⁹, BERNARD GASTINEAU¹⁰, HANS GEISSEL¹³, WILLIAM GELLETLY⁴⁹, JÜRGEN GERL¹³, ROMAN GERNHAUSER³⁹, MIKHAIL S. GOLOVKOV²³, PAVEL GOLUBEV²⁸, ALEXANDER V. GORSHKOV²³, MAGDALENA GÓRSKA¹³, LEONID GRIGORENKO²³, ECKART GROSSE¹¹, JANOS GULYAS⁴, MARIA HAIDUC¹⁸, DUMITRU HASEGAN¹⁸, MICHAEL HEIL¹³, ANDREAS HEINZ⁵², JAN HOFFMANN¹³, MATYAS HUNYADI⁴, ANATOLY V. IGNATYUK²¹, CHERCIU MADALIN ILIE¹³, LENNART ISAKSSON²⁸, BO JAKOBSON²⁸, AKSEL JENSEN¹, HÅKAN JOHANSSON⁸, RON JOHNSON⁴⁹, BJÖRN JONSON⁸, ARND JUNGHANS¹¹, S. KAILAS⁵, RITUPARNA KANUNGO³⁷, ALEKSANDRA KELIC¹³, LINDA KERN³⁸, KHALID KEZZAR¹⁰, ALEXEI KHANZADAEV³⁰, OLEG KISSELEV²⁴, ADAM KLIMKIEWICZ¹³, MARIA KMIECZ¹⁵, IVAN KOJOUHAROV¹³, ALEXEY A. KORSHENINNIKOV³², ATTILA KRASZNAHORKAY⁴, JENS VOLKER KRATZ²⁴, THORSTEN KROELL³⁹, REINER KRÜCKEN³⁹, SERGEY A. KRUPKO²³, REINHARD KULESSA²², NIKOLAUS KURZ¹³, EVGENII A. KUZMIN³², MARC LABICHE⁴⁶, KARL-HEINZ LANGANKE¹³, VALERIE LAPOUX¹⁰, IAN LAZARUS⁷, TUDI LE BLEIS¹³, PHILIPPE LEGOU¹⁰, YVONNE LEIFELS¹³, ROY LEMMON⁷, HORST LENSKE²⁵, ALINKA LEPINE-SZILY⁴⁸, SYLVIE LERAY¹⁰, SIMON LETTS⁷, XIAOYING LIANG⁴⁶, KRIPA MAHATA¹³, ADAM MAJ¹⁶, MIKAEL MEISTER⁸, WOLFGANG MITTIG¹², CHRISTIAN MÜNTZ⁴³, TAKASHI NAKAMURA³⁶, THOMAS NEFF¹³, THOMAS NILSSON⁸, PAUL NOLAN⁴⁴, JERRY NOLEN³, GÖRAN NYMAN⁸, DIEGO OBRADORS⁹, ALEKSEY A. OGLOBLIN³², MAKITO OI⁴⁹, STEFANOS PACHALIS⁴⁴, RUDRAJYOTI PALIT³⁴, NORBERT PIETRALLA³⁸, STEPHANE PIETRI⁴⁹, ZSOLT PODOLYAK⁴⁹, EMANUEL POLLACCO¹⁰, MIHAI POTLOG¹⁸, A PRASAD², VIC PUCKNELL⁷, PATRICK REGAN⁴⁹, RENE REIFARTH¹³, RENE REIFARTH⁴³, PETER REITER⁴², FANNY REJMUND¹², MARIA VALENTINA RICCIARDI¹³, ACHIM RICHTER³⁸, KARSTEN RISSAGER¹, ALEXANDER M. RODIN²³, DOMINIC ROSSI²⁴, PATRICIA ROUSSEL-CHOMAZ¹², BERTA RUBIO¹⁴, TAKEHIKO SAITO¹³, HERVE SAVAJOLS¹², DENIZ SAVRAN³⁸, HEIKO SCHEIT³¹, KARL-HEINZ SCHMIDT¹⁹, CHRISTELLE SCHMITT²⁰, GERHARD SCHRIEDER³⁸, MANOJ K. SHARMA², BRADLEY SHERRILL²⁹, ARADHANA SHRIVASTAVA⁵, SERGEY I. SIDORCHUK²³, CEDRIC SIMENEL¹⁰, HAIK SIMON¹³, JOHN SIMPSON⁷, B.P. SINGH², PUSHPENDRA P. SINGH², KLAUS SPOHR⁴⁶, PAUL STEVENSON⁴⁹, JOACHIM STROTH⁴³, KLAUS SÜMMERER¹³, JOSE L. TAIN¹⁴, ISAO TANIHATA³⁷, STANISLAV TASHENOV¹³, OLOF TENGBLAD⁹, IAN THOMPSON⁴⁹, JEFFREY A. TOSTEVIN⁴⁹, WOLFGANG TRAUTMANN¹³, YURI TUBOLTSEV¹⁹, MANUELA TURRION⁹, STEFAN

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Koll 49: S245-Kollaboration

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Vorträge⁺

Mainz: Jungchemikerforum der Johannes Gutenberg-Universität Mainz, 18.01.2008

M. Piel

Moderne molekulare Bildgebung mittels der Positronen-Emissions-Tomographie

Nierstein: Veranstaltung des Lions Club, 07.02.2008

N. Trautmann*

Segen und Risiko der Kernenergie

Langen: 2. Workshop zur Forschungsinitiative: Validierung humanisierter Maussysteme zur präklinischen Testung am Paul Ehrlich Institut, 22.02.2008

M. Piel

Non-invasive visualisation of human immune cells in NOD-Scid mice using PET

Kaiserslautern: Strahlenschutzkurs, Universität Kaiserslautern, 22.02.2008

H. Keller

Materialien und Einrichtungen für das Radionuklidlabor

H. Keller

Kontamination von Personen und Sachen, Dekontamination

Gießen: 41. Jahrestagung der Deutschen Gesellschaft für Massenspektrometrie (DGMS), 02.-05.03.2008

T. Klimach, S. Amayri, R. Buda, E. Gromm, H. Jungclas, J.V. Kratz, T. Reich, T. Wunderlich
CE-ICP-MS zur Untersuchung des Migrationsverhaltens von Actiniden

Darmstadt: Frühjahrstagung der DPG-Fachverbände Physik der Hadronen und Kerne und Massenspektrometrie, 10.-14.03.2008

K. Boretzky for the R³B-Collaboration
Dipolanregung exotischer Kerne als Zugang zur Dichteabhängigkeit der nuklearen Symmetrienergie

A. Frei, I. Altarev, E. Gutmiedl, G. Hampel, F.J. Hartmann, W. Heil, J.V. Kratz, Th. Lauer, S. Paul, Y. Pokotilovski, Y. Sobolev, M. Urban, N. Wiehl
Production of ultra-cold neutrons with a solid deuterium converter at a test facility at the TRIGA reactor in Mainz

J. Ketelaer, K. Blaum, K. Eberhardt, G. Eitel, S. George, R. Ferrer, F. Herfurth, S. Nagy, W. Nörtershäuser, J. Repp, Ch. Smorra, Ch. Weber
TRIGA-TRAP: A Penning trap setup for mass measurements on exotic and heavy nuclides

J. Krämer

Investigation of 21-Mg by collinear laser spectroscopy and beta-NMR

Th. Lauer, I. Altarev, A. Frei, E. Gutmiedl, G. Hampel, W. Heil, J.V. Kratz, S. Paul, Y. Sobolev, N. Wiehl

Characterization of a solid deuterium ultracold neutron source by the time of flight method

T. Le Bleis for the R³B-Collaboration

Properties of neutron-rich Ni isotopes investigated at LAND

J. Repp, K. Blaum, K. Eberhardt, G. Eitel, R. Ferrer, S. George, J. Ketelaer, S. Nagy, Ch. Smorra, S. Ulmer

Aufbau eines breitbandigen Spiegelstromnachweises für Präzisionsmassenmessungen

S. Raeder, B.A. Bushaw, N. Trautmann, J.V. Kratz, K. Wendt

Hochselektiver Isotopennachweis von Uran-236 mittels HR-RIMS

D. Rossi for the R³B-Collaboration

RPC prototype development for the neutron time-of-flight detector NeuLAND for R³B and EXL at FAIR

R. Sánchez

Frequency Measurements on the 2S-3S Transition of Lithium-7 and Lithium-6

Ch. Smorra, K. Blaum, K. Eberhardt, G. Eitel, R. Ferrer, S. George, J. Ketelaer, D. Liebe, S. Nagy, J. Repp

A carbon cluster ion source for mass calibration of TRIGA-TRAP

Ch. Wimmer for the R³B-Collaboration

Inbetriebnahme der Driftkammern zur Spurverfolgung von Protonen für das R³B-Experiment

Avignon, Frankreich: ACTINET Plenary Meeting, 18.-19.03.2008

S. Amayri, S. Dierking, B. Baeyens, R. Dähn, I. Myers, A. Scheinost, T. Reich
Batch experiments and spectroscopic study of Np(V) sorption on montmorillonite

+ Vortragender unterstrichen, falls nicht an erster Stelle aufgeführt

* auf Einladung

Vancouver (Canada): Halo Workshop, TRIUMF, 27.03.2008

W. Nörtershäuser
Lasers shed new light on halos: The nuclear charge radii of Li-11 and Be-11

Caen, Frankreich: Vortrag am Grand Accelérateur National d'Ions Lourds (GANIL) 28.03.2008

Klaus Eberhardt*
Actinide Target Preparation by Electrodeposition for Fission Induced Reactions and Heavy Ion Studies

East Lansing, USA: Seminar an Michigan State University (MSU), 31.3.2008

C. Geppert
Laser Spectroscopy at GSI

München: Workshop des BMWi-Verbundprojektes "Wechselwirkung und Transport von Actiniden im natürlichen Tongestein unter Berücksichtigung von Huminstoffen und Tonorganika", 01.-02.04.2008

T. Wunderlich
Anwendung der CE-ICP-MS zur Untersuchung der Redoxstabilität des Plutoniums

Essen: Seminar an der Kraftwerksschule Essen (KWS) zur Ausbildung von Reaktoroperatoren, 04.04.2008

K. Eberhardt*
Aufbau, Betrieb und Nutzung des Forschungsreaktors TRIGA Mainz als Neutronenquelle für Forschung und Industrie

Wroclaw, Polen: 38^{èmes} Journées des Actinides, 12.-15.04.2008

S. Dierking, S. Amayri, B. Baeyens, R. Dähn, I. Myers, T. Reich
Macroscopic and EXAFS investigation of Np(V) uptake by montmorillonite

Leipzig: 46. Jahrestagung der Deutschen Gesellschaft für Nuklearmedizin, 23.-26.04.2008

A.N. Bekozob, D.V. Filosofov, N.S. Loktionova, F. Rösch
Combined cation / anion exchange purification of Ge/Ga-68 eluates

M. Herth, F. Debus, M. Piel, M. Planer, P. Riss, G. Knudsen, H. Lüddens, F. Rösch
Synthesis and Evaluation of F-18-MDL 100907, a potential 5-HT_{2A} receptor ligand

P. Reiß, R. Hummerich, P. Schloss, F. Rösch
Synthesis of 16 novel analogues of LBT999 as potent selective dopamine transporter ligands for PET

Mainz: Veranstaltung der Freunde der Universität Mainz e.V., 28.04.2008

G. Hampel*
Der TRIGA Mainz

Bad Berka: 10 Years Anniversary PET and Nuclear Medicine, 02. - 03.05.2008

F. Rösch
Generator-based production of PET radioisotopes

Melbourne, Australien: Seminar im Peter Mc-Callum Hospital, 23.05.2008

F. Rösch*
All you wanted to know about Ga generators but were afraid to ask...

New Orleans, USA: 55th SNM Annual Meeting, 14.-18.06.2008

G. Gründer, F. Rösch, W.M. Schäfer, I. Vernaleken
Quetiapine has a D_{2/3} receptor binding profile similar to clozapine: A [¹⁸F]fallypride PET study in patients with schiziphenia

M. M. Herth, M. Piel F. Debus, M. Palner, F. Rösch
Synthesis and evaluation of 18F-MDL 100907 derivatives for the 5-HT_{2A} receptor

P. Riss, R. Hummerich, P. Schloss, F. Rösch
Conformationally restricted 3-phenyltropanes: Highly selective dopamine transporter ligands for PET

I. Vernaleken, C. Boy, F. Rösch, P. Bartenstein, D.F. Wong, W. Schäfer, G. Gründer
Striatal and extrastriatal D_{2/3}-receptor binding of ziprasidone: Implications of different study schedules

Langen: 3. Workshop zur Forschungsinitiative: Validierung humanisierter Maussysteme zur präklinischen Testung am Paul Ehrlich Institut, 20.06.2008

M. Piel
In vivo gene transfer into cells of the hematopoietic system using cell entry targeted lentiviral vectors

Krakau, Polen: COST BM0607 Action "Targeted Radionuclide Therapy", 24.-25.06.2008

C. Burchardt, P. Reiß, O. Prante, F. Rösch
Ga-68 labeled amino acids

F. Rösch, K. Zhernosekov, D. Filosofov
High specific activities of radiolanthanides following neutron capture nuclear reactions

M. Pruszyński, N. Loktionova, D. Filosofov, F. Rösch
Performance of a 5 mCi Ti/Sc generator

Dijon, Frankreich: Plutonium Future "The Science", 07.-11.07.2008

R.A. Buda, N. Banik, J.V. Kratz, N. Trautmann
The Sorption of Pu(III) and Pu(IV) onto Clay Minerals

Darmstadt, GSI: AP Seminar, 16.07.2008

W. Nörtershäuser
On-line and off-line applications of a frequency comb

Ontario, Canada: International Conference on Precision Physics of Simple Atomic Systems (PSAS 2008), University of Windsor, July 2008

R. Sánchez
Frequency Measurement of the 2S-3S of Li-7 and Li-6

M. Žáková
Towards a Nuclear Charge Radius Determination of the One-Neutron Halo Nucleus ^{11}Be

Budapest, Ungarn: 7th International Conference on Nuclear and Radiochemistry (NRC7), 24.-29.08.2008

S. Amayri, R.A. Buda, D. Fröhlich, J. Heinrich, T. Klimach, J.V. Kratz, T. Reich, N. Trautmann, T. Wunderlich
Sorption of actinides (Th, U, Np, Pu, Am) on Opalinus Clay in synthetic porewater

J.V. Kratz*
Chemistry of the Transactinides

A. Ölcer, J. Drebert, T. Reich
XPS study of electrochemically prepared uranium targets

Lyon, Frankreich: 4th World TRIGA Users Conference, 08.-10.09.2008

G. Hampel, K. Eberhardt
Research with Neutrons of the TRIGA Mainz

Nizza, Frankreich: World Molecular Imaging Conference, 10.-14.09.2008

F. Rösch
From ionic $^{68}\text{Ge}/\text{Ga}$ generators to instant ^{68}Ga labeling chemistry

Ryn, Polen: ENAM08 Conference on Exotic Nuclei and Atomic Masses, 11.09.2008

W. Nörtershäuser
Charge Radius Determination of Halo Nuclei (2005-2008)

Caen, Frankreich: 24th World Conference of the International Nuclear Target Development Society, 15.-19.09.2008

K. Eberhardt, J.V. Kratz, D. Liebe, B. Lommel, M. Schädel, P. Thörle
Preparation of Plutonium Targets for the Gas-filled Recoil Separator TASCA

K. Eberhardt*
The Use of Fission Targets for Chemical and Physical Experiments at the Research Reactor TRIGA Mainz

Mainz: 40. Jahrestagung des Fachverbandes für Strahlenschutz, 15.-18.09.2008

G. Hampel, K. Eberhardt, S. Zauner
Ausbildung und Kompetenzerhalt in Kernchemie, Kernphysik und Strahlenschutz am Forschungsreaktor TRIGA Mainz

Predeal, Rumänien: SPARC2008 Workshop, 23.-28.9.2008

M. Vogel
Precision spectroscopy on trapped highly charged ions

Münster: 16. Arbeitstagung der Arbeitsgemeinschaft Radiochemie / Radiopharmazie, 25.-27.09.2008

M. Herth, M. Barz, M. Jahn, V. Kramer, R. Zentel, F. Rösch
„Click“-Chemie basierte ^{18}F -Glycosylierung eines metabolisch stabilisierten Neurotensin-Derivates: Evaluierung und Kleintier-PET.

T. Capito, V. Bockhart, H. Lüddens, F. Rösch
 ^{18}F -Markierung und Evaluierung α_5 -subtyp-selektiver GABA_A-Rezeptorliganden.

C. Burchardt, P. Riss, O. Prante, T. Kuwert, F. Rösch
 ^{68}Ga -markierte Tyrosinderivate – potentielle Tumortracer für die PET.

Leipzig: 10 Jahre IIF-Festkolloquium, 01.10.2008

N. Trautmann*
Lasermassenspektrometrische und chemische Untersuchungen der schwersten Elemente

La Londe les Maures, Frankreich: Joint Laser-Trapspec workshop 2008, 30.09.-01.10.2008

Z. Andjelkovic
Precision Laser Spectroscopy of HCl in a Penning Trap - the SPECTRAP Experiment

W. Nörtershäuser
High voltage calibration at ISOLDE with collinear laser spectroscopy

D. Tiedemann
Nuclear charge radii of $^{7,10,11}\text{Be}$

Athen, Griechenland: Joint Working Group meeting, 03. – 04.10.2008

C. Burchardt
Gallium-68 labelled amino acids suitable for brain tumor imaging

M. Fellner
Syntheses of ^{68}Ga -schiff base derivatives for in vivo imaging of the p-glycoprotein status in tumours

M. Jahn
Processing of germanium targets for separation of $^{77/72/74}\text{As}$ and labelling chemistry

P. Riss
Direct labelling of natural products with n.c.a. ^{68}Ga : Porphyrins and dchlorins

F. Rösch
Versatile $^{68}\text{Ge}/\text{Ga}$ generator post-processing for ^{68}Ga labelling chemistry

Speyer: Workshop des BMWi-Verbundprojektes "Wechselwirkung und Transport von Actiniden im natürlichen Tongestein unter Berücksichtigung von Huminstoffen und Tonorganika", 07.-08.10.2008

D. Fröhlich
Study of Np(V) sorption on Opalinus Clay and determination of diffusion coefficients of HTO and $^{22}\text{Na}^+$

München, Annual Congress of the EANM 2008, 12.-15.10.2008

H. Amaral, R. Pruzzo, F. Redondo, M. Gil, J. Bolelli, F. Rösch, R. P. Baum
Comparison of PET/CT images with ^{68}Ga -DOTATATE and ^{68}Ga -DOTANOC in Patients with Intestinal Neuroendocrine Tumors: Preliminary Report

Berlin: Seminar an der Bundesanstalt für Materialforschung und -prüfung (BAM) - Training in Metrologie in Chemistry (TrainMic), 23.10.2008

K. Eberhardt*
Chemische Metrologie – wie sicher sind meine Ergebnisse?

Goa, Indien: International Symposium on Radiopharmaceutical Therapy (ISRT-2008), 27-30.10.2008

F. Rösch*
Preparation of ^{68}Ga -labelled tumor imaging tracers

Darmstadt: TASCA-Workshop 31.10.2008

J. Even, J.V. Kratz, M. Mendel, N. Wiehl
Electrodeposition experiments with hassium

New Delhi, Indien: 9th Asia Oceania Congress of Nuclear Medicine and Biology, 31.10.-04.11.2008

F. Rösch*
Effective routes of processing $^{68}\text{Ge}/\text{Ga}$ -radionuclide generators give access to online labelling of new ^{68}Ga radiopharmaceuticals

Florenz, Italien: 13th International Congress on Neutron Capture Therapy, 2.-7.11.2008

G. Hampel, A.L. Aguilar, J. Knorr, S. Minouchehr, S. Nagels, G. Otto, Ch. Schütz, B. Wortmann
Modification of the thermal column of the TRIGA Mainz for the treatment of liver metastasis.

S. Minouchehr, G. Hampel, Ch. Schütz, S. Nagels, S. Altierie, S. Stella, S. Bortolussi, G. Otto
Determination of Boronophenylalanin (BPA) in healthy liver and tumour tissue of patients with liver metastasis of colorectal carcinoma

S. Nagels, F. Becker, G. Hampel, Ch. Schütz, N. Wiehl, B. Wortmann, A.L. Aguilar, G. Otto, S. Minouchehr
Determination of the irradiation field at the research reactor TRIGA Mainz for BNCT

Eilat, Israel: PANIC 2008, 06.-14.11.2008

Ch. Plonka-Spehr
An Improved Neutron Electric Dipole Moment Experiment

Mainz: Veranstaltung des Rotary Clubs, 03.12.2008

G. Hampel*
Kriminalistik, Önologie und Archäologie - Wissenschaftliche Spruensuche im Alltag

Mainz: Festsymposium des Instituts für Kernchemie anlässlich des 70. Jahrestages der Entdeckung der Kernspaltung durch Otto Hahn und Fritz Strassmann und der Verleihung der Honorarprofessur der Universität Mainz an Dr. Norbert Trautmann, 17.12.2008

N. Trautmann*
Die Entdeckung der Kernspaltung am 17.12.1938

Vorträge
im Seminar für Kern- und Radiochemie

- F. Beyerlein (Universität Mainz)
Synthese und nukleophile ^{18}F -Markierung von Tyrosin-Derivaten und aromatischen Modellverbindungen
- A. Borschevskii (Universität Tel Aviv)
Fully relativistic ab initio calculations of the properties of the 7p elements and predictions of their experimental behaviour
- P. Campell (University of Manchester)
Electrostatic and optical manipulation of cooled radioactive ions for nuclear spectroscopy
- F. Debus (Psychiatrische Klinik, Universität Mainz)
Tier-PET Mainz: Infrastruktur und aktuelle Forschungen
- S. Dierking (Universität Mainz)
Sorption von Np(V) an $\gamma\text{-Al}_2\text{O}_3$ und Montmorillonit
- R. Eichler (PSI / Villigen)
Adsorptionsuntersuchungen mit den Superschweren Elementen 112 und 114
- R. Eichler (PSI / Villigen)
Yoctochemistry – Mission imponderable
- Ch. Düllmann (Universität Mainz)
Physikalisch vorseparierte schwere Elemente – Rohstoffe für vielfältige chemische und physikalische Studien im Grenzbereich
- J. Even (Universität Mainz)
Unterpotentialabscheidung von Ruthenium und Osmium
- V. Ezhov (Petersburg Nuclear Physics Institute, Gatchina)
Measurement of the free neutron lifetime in a magnetic storage bottle
- M. Feige (Universität Mainz)
Untersuchungen zum zeitlichen Verlauf der Elementkonzentrationen während der Traubenreife und der Mostfermentation mittels Neutronenaktivierungsanalyse
- D. Fröhlich (Universität Mainz)
Untersuchungen zur Sorption von Neptunium an Opalinuston
- D. Gabel (Universität Bremen)
Die Strahlenbiologie der Bor Neutroneneinfangtherapie und ihre Folgen
- J. Hooker (Brookhaven National Laboratory USA)
The use of Carbon-11 Chemistry to Study Psychoactive Drugs
- O. Keller (Universität Mainz)
Neue Detektorelektronik
- G.M. Knudsen (Copenhagen University Hospital)
Pre- and post-synaptic mapping of the serotonin system
- V. Kramer (Universität Mainz)
Synthese, ^{18}F -Markierung und Evaluierung von MDL 100907-Derivaten zur Visualisierung von Veränderungen der endogenen Serotoninkonzentration
- J. Mibus (PSI / Villigen)
Diffusion von organischen Makromolekülen in tonigen Medien
- S. Reber (Fraunhofer Institut für Solare Energiesysteme, Freiburg)
Waferäquivalente: Kostengünstige Photovoltaik basierend auf metallurgischem Silicium
- A. Reimer-Müller (TU München)
Untersuchungen zur UCN-Produktion in festem Deuterium
- Y. Pokotilovski (JINR, Dubna)
Options for neutron lifetime measurements in material traps
- A.V.R. Reddy (Radiochemistry Division, B.A.R.C. / India)
Large Sample Neutron Activation Analysis and Prompt Gamma Neutron Activation Analysis
- N. Scheid (Universität Mainz)
Kriminaltechnische Untersuchung von Ziegelsteinen: Methodenvergleich zwischen Laser-Ablation-induktiv gekoppelte Plasma-Massenspektrometrie, Neutronenaktivierungsanalyse und Röntgenfluoreszenzanalyse

C. Schütz (Universität Mainz)
*Borbestimmung in Gewebeproben im Rahmen der
Entwicklung eines Behandlungsprotokolls für die
Bor-Neutronen-Einfangtherapie an einer autotrans-
plantierten Leber*

K. Schreckenbach (TU München)
Die Positronenquelle Nepomuk am FRM-II

D. Schumann (PSI / Villigen)
Wässrige Chemie von Transaktiniden

J. Sterba (Atominstytut Wien)
*Neueste Entwicklungen auf dem Sektor Kurzzeitakti-
vierungsanalyse mit automatisierter konsekutiver
Spektrenaufnahme*

D. Tiedemann (Universität Mainz)
*Bestimmung der Kernladungsradien von Be-7,9,10
und des Halokerns Be-11*

A. Türler (TU München)
Ein Steifzug durch die Nuklidkarte

C. Walther (FZ Karlsruhe, Institut für Nukleare Ent-
sorgung)
Speziation von Actinoiden in aquatischen Systemen

C. Walther (FZ Karlsruhe, Institut für Nukleare
Entsorgung)
*Polymerisierung vierwertiger Actinoid-Ionen in
Lösung - von der Hydrolyse zur Kolloidbildung*

E. Weber (Fraunhofer Institut für Solare Energiesys-
teme)
*Regenerative Energie - Forschung am Fraunhofer
Institut für Solare Energiesysteme*

A. Yakushev (TU München)
Experimental Development in SHE Chemistry

Beiträge der Dozenten des Instituts zu den Lehrveranstaltungen des Fachbereichs Chemie und Pharmazie (SS 08 und WS 08/09) sowie zur Weiterbildung

Vorlesungen, Seminare, Kurse und Praktika in Kernchemie:

Einführung in die Kernchemie (mit Übungen)	J.V. Kratz
Chemie und Kernchemie der schwersten Elemente	Ch. Düllmann
Kernreaktionen	J.V. Kratz
Fundamentale Experimente mit ultrakalten Neutronen	W. Heil, J.V. Kratz
Radiopharmazeutische Chemie	F. Rösch
Moderne Experimente der Atomphysik	W. Nörtershäuser
Physik des Lasers	W. Nörtershäuser
Fundamentale Experimente mit ultrakalten Neutronen	Ch. Plonka-Spehr
Einführung in die Kosmochemie III + IV	U. Ott
Modul Kernchemie I	J.V. Kratz, F. Rösch, T. Reich, Ch. Düllmann, W. Nörtershäuser, G. Hampel, H. Keller, K. Eberhardt, M. Piel
Modul Kernchemie II	J.V. Kratz F. Rösch T. Reich M. Piel
Modul Radiopharmazeutische Chemie I	F. Rösch G. Dannhardt M. Piel
Modul Radiopharmazeutische Chemie II	F. Rösch G. Dannhardt W. Kiefer M. Piel
Seminar über laufende Arbeiten im Institut für Kernchemie	J.V. Kratz F. Rösch T. Reich W. Nörtershäuser Ch. Plonka-Spehr

Seminar für Kern- und Radiochemie	J.V. Kratz F. Rösch T. Reich W. Nörtershäuser Ch. Plonka-Spehr
Seminar über aktuelle Themen aus der Kosmochemie und Astrophysik	U. Ott K.-L. Kratz
Kernchemisches Praktikum I (36 Teilnehmer)	J.V. Kratz F. Rösch T. Reich
Kernchemisches Praktikum II (8 Teilnehmer)	J.V. Kratz F. Rösch T. Reich Ch. Plonka-Spehr
Projektarbeiten zu Masterstudiengängen (2 Teilnehmer)	G. Hampel
Grundkurs im Strahlenschutz zum Erwerb der Fachkunde nach § 30 Strahlenschutzverordnung (13 Teilnehmer)	H. Keller J.V. Kratz F. Rösch sowie weitere Referenten
Aktualisierung der Fachkunde im Strahlenschutz (3 Teilnehmer)	H. Keller
Kurs Fachkunde im Strahlenschutz für Lehramtskandidaten der Chemie und Physik (unter Mitwirkung des Ministeriums für Umwelt und Forsten, Mainz) (71 Teilnehmer)	G. Hampel K. Eberhardt H. Keller sowie weitere Referenten
Reaktorpraktikum (16 Teilnehmer)	G. Hampel K. Eberhardt H. Keller
Internationaler Studienaustausch (3 Teilnehmer)	F. Rösch M. Piel J. Fowler
Praktikum Physiklaboranten im Bereich der Instrumentellen Neutronen-Aktivierungsanalyse (2 Teilnehmer)	G. Hampel
Reactortraining course for the University of South Carolina (8 Teilnehmer)	G. Hampel

Mitwirkung an Diplomprüfungen, in denen Kernchemie als viertes Fach gewählt wurde:
58 Prüfungen

Mitwirkung an Wiederholungsprüfungen Diplom Chemie, Physik
7 Prüfungen

Mitwirkung an Promotionen, in denen Kernchemie als Haupt- oder Nebenfach gewählt wurde:
6 Prüfungen

Lehrveranstaltungen in Chemie:

Vorlesung Chemie für Physiker, Geologen und Mineralogen I T. Reich
(mit Übungen)

Vorlesung Chemie für Physiker, Geologen und Mineralogen II S. Amayri
(mit Übungen)

Allgemeines anorganisch-chemisches Praktikum für
Geologen und Mineralogen
(36 Teilnehmer)

T. Reich
sowie weitere Assistenten

Allgemeines anorganisch-chemisches Praktikum für
Physiker und Meteorologen
(7 Teilnehmer)

T. Reich
sowie weitere Assistenten

Vordiplom in Physik (Fach: Chemie):

54 Prüfungen

Vordiplom in Geologie-Paläontologie (Fach: Chemie):

31 Prüfungen