

The Laboratory of Radiochemistry at Bern University and the Paul Scherrer Institute

Heinz W. Gäggeler*^{a,b} and Urs Krähenbühl^a

Abstract: Radiochemical research in Switzerland is pursued in a laboratory jointly financed by Bern University and the Paul Scherrer Institute. Presently, four groups – one at Bern University and three at the Paul Scherrer Institute – perform basic research in heavy element chemistry, atmospheric chemistry, paleoatmospheric studies, and geochemistry. While the first topic resembles frontier research in radiochemistry, the latter three activities involve the use of radiotracers in several environmental research fields. Most of the experiments require access to the accelerator systems and the spallation neutron source at the Paul Scherrer Institute. Some recent results of the four groups are summarized. They include the first ever chemical study of hassium (element 108), the application of the positron emitter ^{13}N for atmospheric studies, the reconstruction of the pollution history over Europe and some radioanalytical studies with meteorites.

Keywords: AMS-applications · Heavy elements · Nuclear dating · Positron emitters · Radiochemistry

Since 1993 Bern University and the Paul Scherrer Institute have supported a joint laboratory to carry out basic and applied research in radiochemistry and to educate and train students in this field. The University of Bern is unique in Switzerland in offering radiochemistry as a discipline. The research activity of the laboratory is summarized in annual reports (see <http://dcb-radio1.unibe.ch>).

In the following some remarks are made why expertise in radiochemistry is still much needed in Switzerland, followed by a short description of the research activities presently carried out by our laboratory.

Why Radiochemistry?

Application of radioactive isotopes is an important tool in many research fields and also serves to monitor industrial processes. Moreover, there is an increasing demand for radio-labelled compounds from the life sciences.

Nuclear techniques are instrumental in applications dealing with the determination of ultra trace concentrations – even down to the one atom level. Studies of the heaviest elements at the end of the periodic table belong especially to this field. Radiochemical methods have largely contributed to help understand processes in cosmochemistry and geochemistry. Moreover, dating with naturally occurring radioisotopes have become an indispensable tool in archaeology, geology and other fields. These isotopes are produced either by spallation reactions (e.g. ^{14}C via interaction of cos-

mic rays with nitrogen in the upper atmosphere) or are primordial, *i.e.* still exist on Earth due to their long half-lives such as ^{238}U or ^{232}Th .

Many biological secrets could only be unravelled by the employment of radioactive isotopes. Studies of metabolism have profited largely from the use of molecules labelled with radioisotopes such as T, ^{14}C , ^{35}S or ^{32}P . Similarly, the application of $^{99\text{m}}\text{Tc}$ has developed to a 'work horse' in nuclear medicine. Positron-emitting short-lived radionuclides such as ^{18}F in connection with PET-scanners offer challenging novel diagnostic means and precision.

The fact that our society continues to rely on electricity production by nuclear power plants demands well-trained personnel with a basic knowledge in radiochemistry. With the new ideas about nuclear energy production by means of accelerator-driven systems, a totally new field could open up where knowledge in radiochemistry would be much required.

On the other hand, application of radio-tracers as well as energy production *via* nuclear fission generates many different forms of radioactive waste. The safe handling of this waste and its proper conditioning for final storage is a de-

*Correspondence: Prof. Dr. H.W. Gäggeler
^aDepartment of Chemistry and Biochemistry
University of Bern
Freiestrasse 3
CH-3012 Bern
Tel.: +41 31 631 42 64
Fax: +41 31 631 42 20
E-Mail: heinz.gaeggeler@iac.unibe.ch
<http://dcb-radio1.unibe.ch>
^bPaul Scherrer Institute
CH-5232 Villigen

manding task for specialists trained in radiochemistry. Also the projects on nuclear waste transmutation could offer unique opportunities to help solve the nuclear waste problem by totally new means.

In the following, some examples of ongoing research activities of the Laboratory of Radiochemistry are outlined.

Chemical Properties of Heaviest Elements

The synthesis of elements heavier than the actinides allows the limits of the periodic table to be probed. In particular, deviations of the periodicity of chemical properties for heaviest elements are predicted as a consequence of increasingly strong relativistic effects on the electronic shell structure. The transactinides have now been extended up to atomic number 116, but chemical properties have only been investigated up to element 108 (hassium, Hs) [1]. Our group has pioneered the application of isothermal gas chromatography as a tool for studying transactinides. This includes the development of a novel chemical separator OLGA (On-Line Gas chemistry Apparatus) [2] that can be coupled directly to a heavy ion accelerator. Due to its high efficiency and separation speed, nuclides with half-lives as low as one second can be separated and detected at a level of about one produced atom per day of beam time. To serve the needs of such investigations, the Paul Scherrer Institute has implemented a new ECR (electron cyclotron resonance) ion source at its PHILIPS cyclotron. With this ion source, highly charged heavy ions can be injected and accelerated with high intensities.

The first transactinides are 6d elements, hence gas chemical separation procedures at maximum temperatures of about 1000 °C require, first, the synthesis of volatile molecules. For the elements rutherfordium (Rf, $Z = 104$) and dubnium (Db, $Z = 105$) the pure halides (chlorides and bromides) are ideal for this purpose [3]. The next elements seaborgium (Sg, $Z = 106$) [4] and bohrium (Bh, $Z = 107$) [5] can be most easily separated in the form of their oxyhalides (e.g. oxychlorides). For the very recently studied element hassium, the tetroxide was the molecule of choice. All these transactinides have been investigated at a level of a few atoms per experiment. As an example, on the basis of six detected atoms, in the most recently investigated first ever chemical investigation of hassium it was possible to show that HsO_4 is formed

with oxygen at elevated temperatures but is slightly less volatile than OsO_4 . This observation enables hassium to be positioned in the periodic table in group 8, *i.e.* below Os. Fig. 1 summarizes measured retention times (*i.e.* yields) for RfCl_4 , DbCl_5 , SgO_2Cl_2 , and BhO_3Cl , respectively, in empty quartz columns as a function of temperature [6]. The conversion of yield *vs.* time is performed using the decay time of the radionuclide as a clock. At relative yield values of 25%, 50%, or 75% for example, the retention times are 2, 1, or 0.5 half-lives of the radionuclide. The HsO_4 experiment was based on a different technique where the deposition temperature in a thermochromatography detector array (COLD) was measured.

Future efforts will concentrate on the recently discovered spherical superheavy elements with atomic numbers 112, 114 and 116 (as yet unnamed) [7] rather than continuing with meitnerium (Mt, $Z = 109$). The reason is that no sufficiently long-lived isotopes of Mt are known to exist for chemical study. For the heavier elements, thanks to new magic nucleon shells at the proton number $Z = 114$ and neutron number $N = 184$, relatively long-lived nuclides (half-lives much longer than one second) are known to exist.

Surface Chemical Studies with Short-lived Isotopes

The application of radiotracers offers unique opportunities to study chemical reactions at a trace level. This technique approaches the highest possible sensitivity if short-lived isotopes are used that can be detected at the 'one-atom(or one-molecule)-at-a-time' level.

With accelerators and the spallation neutron source SINQ from the Paul Scherrer Institute short-lived positron emitters (e.g. ^{13}N) or fission-products (e.g. ^{84}Br) can be synthesized and transported to a chemistry laboratory.

The main focus of this research is in heterogeneous atmospheric chemistry because current techniques aimed at studying heterogeneous reactions under realistic conditions are often subject to restrictions caused by the low amount of material present in the observed processes. Especially the application of ^{13}N as tracer has yielded valuable new insights into several important aspects such as the heterogeneous production of nitrous acid on soot in polluted air masses [8]. More recently, reversible adsorption of ^{13}N and surface reaction of

^{13}N on solid NaCl surfaces was investigated [9].

In addition, the application of short-lived bromine isotopes opens up new perspectives in the investigation of brominated species with aerosol particles, *e.g.* in the context of arctic ozone depletion studies [10].

Paleoatmospheric Investigations

Archives such as glaciers are ideally suited to the preservation of air from the past. High-altitude glaciers from the Alps have been used to reconstruct the pollution history of Western Europe during the industrialization period, *i.e.* back to about 1850 [11][12] (Fig. 2 [13]). More recently, glaciers from the Andes were analyzed to reconstruct the history of the El Niño phenomenon. Finally, in an ongoing project, glaciers from the Altai mountains serve to reconstruct heavy metal and radioactive plutonium contamination in Siberia due to mining activities and nuclear weapons testing from the nearby Semipalatinsk test-site in Kasachstan.

All these studies involve application of nuclear techniques as well as conventional analytical means. Based on ^{210}Pb measurements, ice archives may be dated back to about 1850. On the other hand, accelerator mass spectrometric (AMS) measurements of ^{14}C , ^{10}Be , ^{36}Cl , ^{129}I or ^{239}Pu yield interesting information on environmental processes. Such measurements are performed at the tandem accelerator in Zürich, jointly operated by the ETH and the Paul Scherrer Institute.

Research with Meteorites

Another application of AMS is the investigation of production rates of ^{10}Be for dating meteorites. For measurement of this isotope it is necessary to separate very small amounts of beryllium from rather large sample masses. The goal of this separation is the complete removal of the interfering boron, which has also an isotope of the same mass, ^{10}B , with a natural abundance of 80%. Since the abundance of B is much higher than Be in the samples under investigation, a necessary separation factor between the elements of at least 10^8 is required [14].

In another project the separation of Cr and Mn is investigated for the measurement of ^{53}Mn . This isotope is produced from iron in meteorites by cosmic radiation. For the measurements of ^{53}Mn with HR-ICP-MS (high-resolution inductively

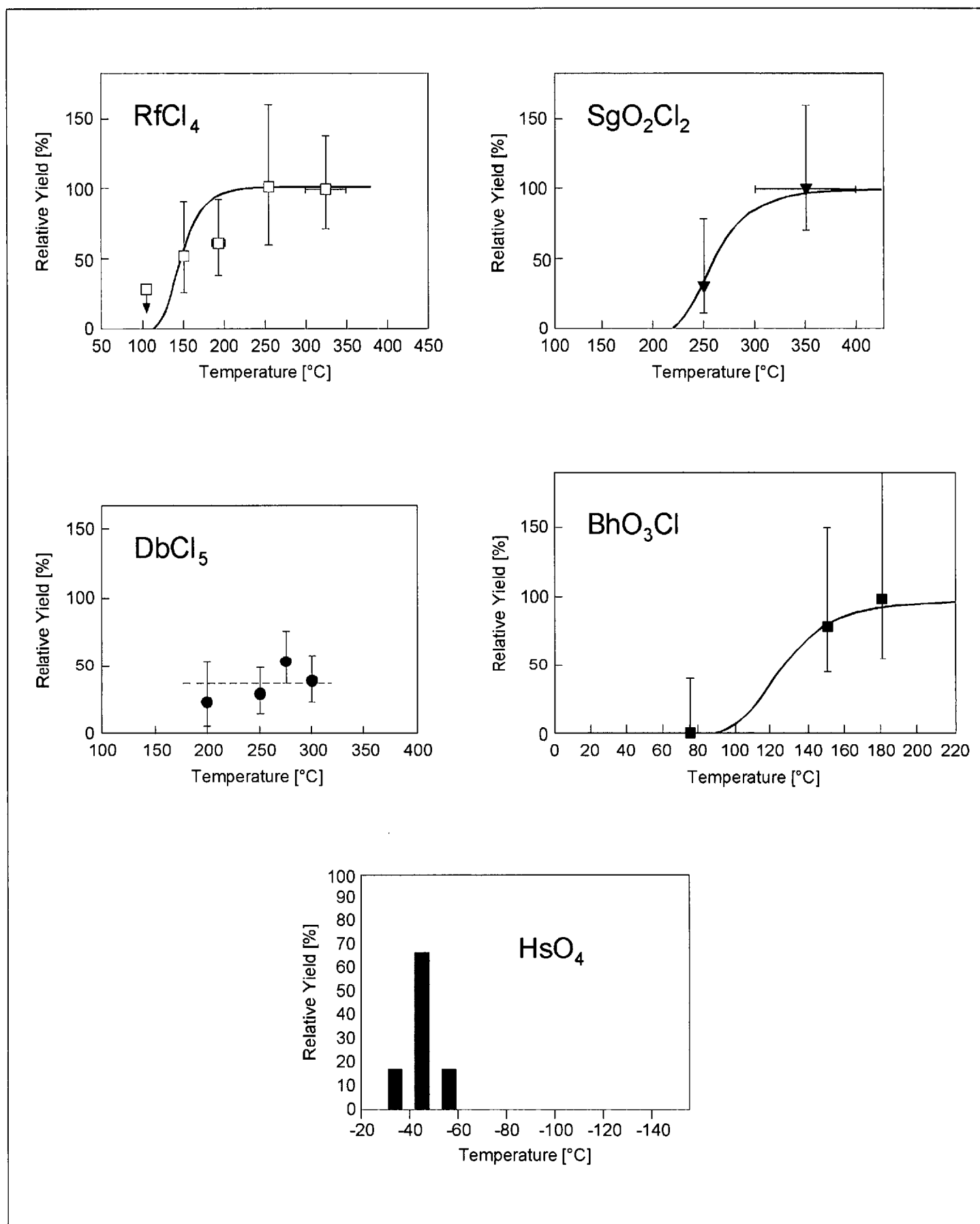


Fig. 1. Measured retention temperatures of volatile chlorides of rutherfordium ($Z = 104$) and dubnium ($Z = 105$), oxychlorides of seaborgium ($Z = 106$) and bohrium ($Z = 107$), and oxides of hassium ($Z = 108$) in quartz columns from several experiments (see [5][6]) using the on-line gas chemistry apparatus OLGA for Rf, Db, Sg, Bh [2] and the thermochromatography detector device COLD for Hs (see [1]).

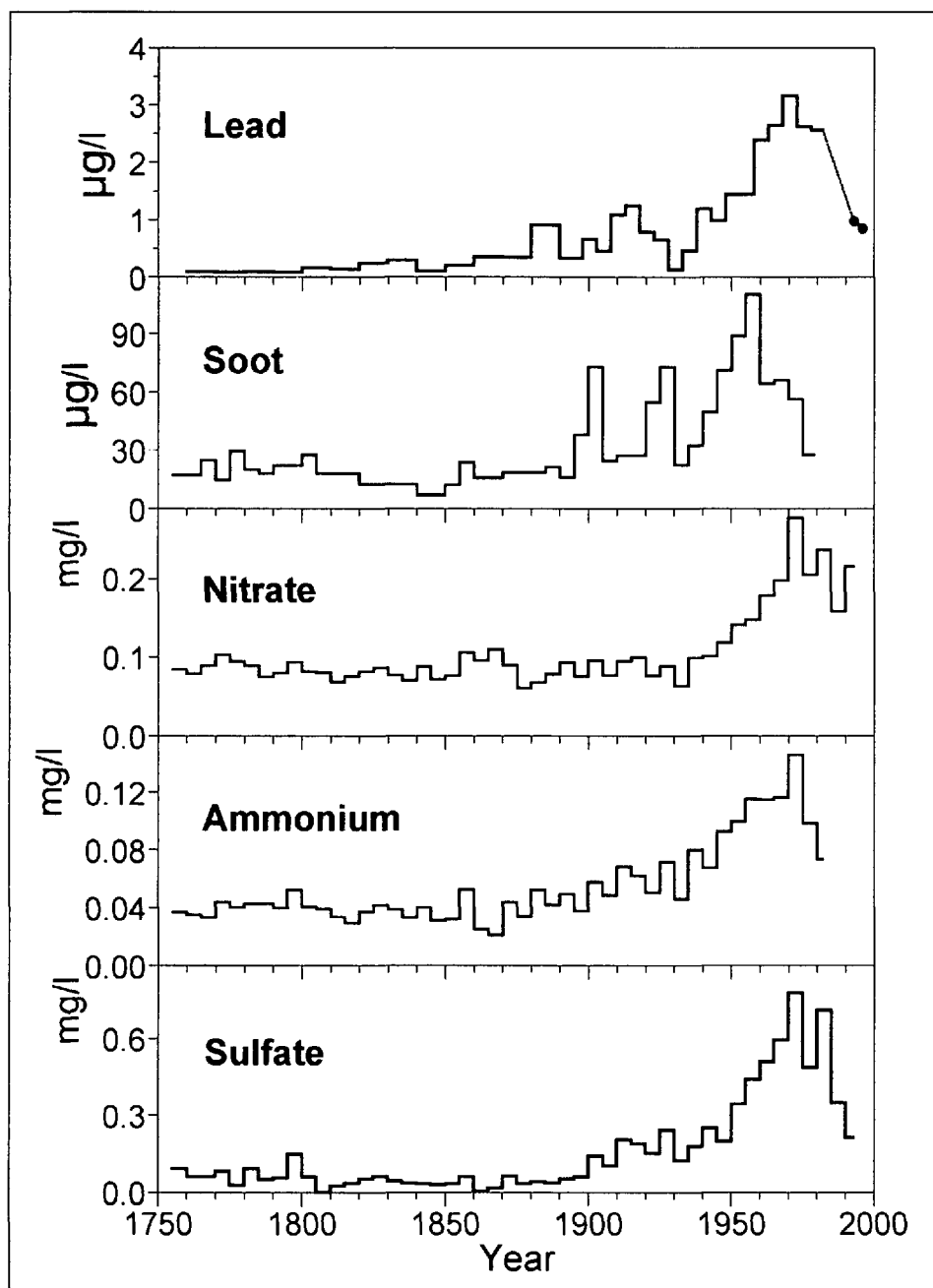


Fig. 2. Historic trends of several ionic species (sulphate, nitrate, ammonia, lead) and of soot deduced from the chemical analysis of high-alpine glacier ice cores from Colle Gnifetti (4450 m asl) and Fiescherhorn (3900 m asl), both situated in the Swiss Alps. Every species represents a different emission source (from [13]).

coupled plasma mass spectrometry) a separation factor between Mn and Cr of 10^8 to 10^{10} is required. This goal was achieved in a separation on a cation-exchange resin using nitric acid as eluent and liquid-liquid extraction applying PAN (pyridylazo-anphthol) as ligand in chloroform [15].

Applied Radiochemistry

Two additional groups of our laboratory are engaged in R&D work for nuclear facilities. This includes the development of procedures for the conditioning

of nuclear waste samples for final storage in a medium-level nuclear waste repository. Also the application of accelerators in research and many applied fields (e.g. medicine) produces nuclear waste that has first to be analyzed prior to transfer to a repository. Within the European project EURISOL target chemical problems are studied for a future radioactive beam facility. All these applied projects need radiochemists with profound knowledge of nuclear physical processes that produce these radionuclides as well as in analytical chemistry.

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