Negative thermal ionization mass spectrometry of selenium
Part 4. Selenium trace determination in sediments and related samples*

Klaus G. Heumann and Manfred Wachsmann
Institut für Anorganische Chemie der Universität Regensburg, Universitätsstrasse 31, D-8400 Regensburg, Federal Republic of Germany

Summary. Selenium traces have been determined in different sediments (estuarine, river, lake), sandy soil and sewage sludge with isotope dilution mass spectrometry (IDMS). Negative selenium atomic ions are formed in a double-filament thermal ion source. The use of a silica gel technique for ionization improves the mass spectrometric sensitivity by a factor of 40 compared with the technique previously applied. An enriched $^{82}$Se spike is used for the isotope dilution process. The samples are decomposed with a mixture of conc. HNO$_3$ and conc. HF. After decomposition selenium is separated by the formation of SeH$_2$ in a hydride generation system which is normally applied for atomic absorption spectrometry. The IDMS results for three standard reference sediments agree well with the certified values. In the case of three other standard reference materials, which are not certified for selenium up to now, the IDMS analyses were able to improve the selenium data given for information or as indicative values. The precision of the IDMS method in the concentration range of 0.2 - 3.5 µg/g lies between 0.8% and 4.1%. The detection limit is 6 ng/g. A comparison with several other methods shows that IDMS is one of the very few analytical methods which produces accurate selenium results even at concentration levels of 0.2 µg/g and less in sediments and related samples of environmental interest.

Introduction
The importance of analyses of the essential trace element selenium is well known and has been discussed in a number of papers, e.g. by Tölg and co-workers [1, 2]. While hydride generation atomic absorption spectrometry (HGAAS) is the most frequently used method for selenium determinations, it is useful to have alternative methods for comparison as a control of the accuracy of analytical results. We therefore developed a definitive method of isotope dilution mass spectrometry (IDMS) to determine selenium traces in different important matrices using the negative thermal ionization (NTI) technique. In a series of publications about NTI-MS of selenium we have described the total selenium and selenium species determination in aquatic systems [3, 4] and the selenium analysis in food samples [5].

The determination of selenium with HGAAS is influenced by the presence of different heavy metals [6-8]. Because sediments and other samples of environmental interest very often contain relatively high concentrations of these metals a careful elimination of interferences must be carried out when using HGAAS [9]. If less attention is paid to this topic, inaccurate results are the consequence as it has been the experience of a number of interlaboratory studies. We therefore describe a NTI-IDMS technique in this paper which is able to produce relatively accurate selenium results in sediments and related samples of environmental interest (soils, sewage sludges, etc.).

With the new IDMS method we determined three standard reference materials (Estuarine Sediment NBS 1646, Light Sandy Soil BCR 142, Sewage Sludge BCR 145), where no certified values for selenium have been given up to now. We additionally took part in the certification campaign for the certification of three different sediments by the Community Bureau of Reference in Brussels.

Experimental
Isotope ratio measurements of Se with NTI-MS
During the last few years the formation of negative thermal ions on the surface of a hot metal filament has increasingly been used for isotope ratio determinations [10]. The principles and advantages (selective ionization method, relatively high ion intensities, only a few interferences) of this ionization technique have been described elsewhere [11]. For the isotope ratio determination of selenium we used a technique described in [3, 12] in our previous investigations. Due to the high sensitivity, which was necessary for the analysis of small amounts of selenium in some of the sedimentary samples, we improved the NTI technique for selenium [13].

A double-filament ion source (filaments consist of rhenium) and a silica gel suspension were used for the new technique. The dried selenium sample is first mixed with 10 µl of the silica gel suspension, which is prepared by a procedure described by Barnes and co-workers [14]. Afterwards, this mixture is deposited on the evaporation filament where it is evaporated to dryness. We believe that the silica

* Dedicated to Prof. Dr. G. Tölg on the occasion of his 60th birthday
Offprint requests to: K. G. Heumann

gel prevents the evaporation of selenium at a temperature too low for sufficient formation of $\text{Se}^{-}$ ions by the ionization filament. 30 $\mu$g barium in form of a barium hydroxide solution is deposited on the ionization filament and evaporated to dryness to decrease the electron work function of the filament material and thus to increase the negative thermal ion current [11]. Using this technique $\text{Se}^{-}$ ion currents of approximately $10^{-11}$ A could be observed at the detector side of a thermal ionization mass spectrometer when a sample amount of 0.5 $\mu$g selenium and ionization filament temperatures of 940–990 °C were used. This is an increase in the selenium ion current of a factor of about 40 compared with the previously applied NTI method.

The mass spectrometric measurements of this work were carried out with two different magnetic sector field instruments, type CH5-TH and MAT 261 (both Finnigan MAT). The principles of IDMS for selenium determinations have been described in the first part of this series of publications [3]. The same HNO$_3$ acidic $^{82}$Se selenite spike solution (pH = 1) as was used for selenium analyses in food samples [5] could be applied in this work. The concentration of this spike was $(1.179 \pm 0.002) \times 10^{17}$ selenium atoms per gram of solution and the two isotopes used for the isotope ratio determination have abundances of $^{80}\text{Se} = 5.34\%$ and $^{82}\text{Se} = 91.18\%$, respectively.

**Sample treatment**

Because sediments, soils and related samples contain more or less high portions of silicate, hydrofluoric acid must be used for a total dissolution of these matrices. 0.1 – 1.2 g of the sample, depending on the selenium concentration, is weighed into a Teflon vessel which can be used — after placing this vessel into a steel bomb — for decomposition under pressure. An exactly weighed amount in the range of 0.4 – 1 g of the spike solution is added. Because the spike is a HNO$_3$ acidic solution (pH = 1) the carbonates of the sample are already decomposed at this step of the analytical procedure. After the CO$_2$ emission has finished 1 ml bidist. H$_2$O, 10 ml conc. HNO$_3$ (p.a.) and 10 ml HF (40%, supra-pure) are added. The vessel is then closed with a Teflon cap, placed into the steel bomb and heated up to 150 °C in a hot-air cabinet for 5 h. After cooling the opened vessel is placed into an electrically heatable aluminium block which contains boreholes with a diameter suitable for the vessels. The solution is then evaporated to dryness at a temperature of 120 °C.

The next analytical steps are identical with those we applied for the analysis of selenium in food samples [5]. The reduction of Se(VI) to Se(IV) is carried out by adding 20 ml 5 mol/l HCl (supra-pure) into the Teflon vessel. Selenium is then separated by the formation of SeH$_2$ in a hydride generation system normally used for HG-AAS analyses (system BSH 951, Berghof; NaBH$_4$ solution 3% by weight, Ar carrier gas flow of 4–6 l/h.

SeH$_2$ is absorbed in conc. HNO$_3$ using an absorption tube which was especially constructed for this purpose (see [5]). Investigations with a radioactive $^{75}\text{Se}$ tracer have shown that the recovery of selenium for the SeH$_2$ formation and absorption step is about 48% in average, which is evidently lower than for the similar procedure with food samples [5]. However, one main advantage of IDMS is that — after the isotope dilution step with the spike has taken place — losses of the element to be determined do not influence the analytical result. A low selenium recovery only reduces the sensitivity of the method which is compensated in this work by the development of a much more sensitive mass spectrometric technique.

After evaporating the absorber solution to dryness the residue is mixed with 10 $\mu$l of a silica gel suspension and then deposited on the evaporation filament of the thermal ionization mass spectrometer for the $^{80}\text{Se}/^{82}\text{Se}$ isotope ratio measurement.

**Results and discussion**

The selenium results with IDMS in three different standard reference sediments are listed in Table 1. The certified values are also given for comparison. The relative standard deviations of the IDMS analyses, obtained from 5 – 7 independent determinations of each sample, are in the range of 1.5 – 4.1%. The highly reproducible result of the lake sediment with the lowest selenium concentration in the ng/g level demonstrates the potential of the IDMS method. The IDMS values agree well in all cases with the certified values within the given uncertainties.

The detection limit of the IDMS method is limited by the variation of the blank for the described analytical procedure. In 9 independent runs the blank was determined to be $(9 \pm 2)$ ng. This means that in the case of a weighed sample of 1 g the detection limit lies at 6 ng/g $(3 \times 8$ definition). Due to the normal distribution of selenium in the environment it should be possible to determine this element in all sediments and related samples with IDMS. Because IDMS is a definitive method the results should be relatively accurate as well.

The estuarine, river and lake sediments were analysed with IDMS within a certification campaign organized by the Community Bureau of Reference in Brussels. The results of this certification round are summarized in Table 2. The listed concentration ranges (minimum and maximum means of all participating laboratories) show that the results differ by a factor of 2.1 – 3.3. This discrepancy in the analytical results makes the necessity for calibration obvious, e.g. by the use of a definitive method like IDMS.

The results of 9 and 8 participating laboratories could be accepted for certification in case of the estuarine and river sediment. In the case of the lake sediment only the results of 4 laboratories were adequate for certification. Radiochemical neutron activation analysis (RNAA), different modes of AAS, a fluorimetric method (FLU), X-ray fluorescence spectrometry (XRF) and our IDMS method were applied during this certification campaign. It was stated in the certification report [15] that for a sediment matrix and

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration [µg/g]</th>
<th>IDMS</th>
<th>Certified value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estuarine sediment BCR 277</td>
<td>2.03 ± 0.06</td>
<td>2.04 ± 0.18</td>
<td></td>
</tr>
<tr>
<td>River sediment BCR 280</td>
<td>0.73 ± 0.03</td>
<td>0.68 ± 0.06</td>
<td></td>
</tr>
<tr>
<td>Lake sediment BCR 320</td>
<td>0.198 ± 0.003</td>
<td>0.214 ± 0.034</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Selenium determination in three different standard reference sediments with IDMS.