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Heinrich Baumann**

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Another application is concerned with the determination of toxic heavy metals in iron oxides. Those iron oxides are the by-

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One application shown is the determination of traces of Pt-group metals in pharmaceuticals and agrochemicals. Ru, Rh, Pd, and Pt are used as hydrogenating catalysts. Catalyst losses have to be controlled because of economical and ecological reasons. After digesting the samples with HNO_3/HCl in a *Carius* tube, detection limits in the lower ng/g range can be reached for those metals.

Another application is concerned with the determination of toxic heavy metals in iron oxides. Those iron oxides are the by-

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products of different reduction processes. As they are to be given to the cement industry for disposal, the tolerated concentrations of some heavy metals such as Cd, Hg, Tl, and Pb must not be higher than 1 to 2 µg/g. The required detection limits can easily be reached by dissolving the iron oxides in HNO_3/HCl and diluting the resulting solutions till their Fe contents are below 1000 µg/ml.

Tetraalkyltin compounds are known to be very toxic. For ecotoxicity tests, the concentrations down to 50 pg/ml have to be determined in nutrient solutions for algae and daphnia. The nutrient solutions can be measured directly, *i.e.* without any sample preparation.

As another example for an ultratrace analysis, the determination of U and Th in the pg/g range in high-purity quartz and photoresists for the production of semiconductor materials is described. Suitable sample preparation procedures for these analyses are the digestion with $HF/HNO_3/H_2SO_4$ in *Teflon* vessels, and the decomposition by means of a radio-frequency-induced oxygen plasma in a cool plasma asher, respectively.

Se is an element which cannot be detected so well by Ar-ICP-MS. Because of its high ionization potential, the ionization degree is rather low in the Ar plasma. Additionally, the main isotopes are interfered by molecular ions such as $ArAr^+$ and, in the presence of chlorine in the solution, $ArCl^+$. A He-supported plasma, therefore, might offer an interesting alternative. In this paper, we report some results of the determination of Se traces in silver nitrates. For these determinations, mass spectrometric isotope dilution analysis (MS-IDA) is employed. After the addition of a ^{82}Se spike to a solution of the silver salt, silver is precipitated as AgCl. The Se isotope ratio in the remaining solution is measured. The results obtained with an Ar-ICP-MS and a He-MIP-MS are compared. With the He plasma, sample preparation is easier and lower detection limits can be achieved.

1. Introduction

Today, product development, quality assurance, and environmental protection control depend on reliable high-quality analytical data more than ever before. The need for determining elements present in trace amounts at the ppm or ppb level called for improved analytical methods. One of the newest and most promising methods for multi-element determinations in the extreme trace region is Inductively Coupled Plasma Mass Spectrometry (ICP-MS). After the first publication on ICP-MS describing work done by *Houk et al.* in collaboration with *Gray* at Ames laboratory at Iowa State University in 1980 [1], commercial instruments were soon available. Today, approximately 350 ICP-MS instruments have been installed all over the

world. Despite this rapid success of the method, there are still doubts about the benefits of ICP-MS as a routine method for an industrial laboratory. The present publication tries to demonstrate what this relatively new method may accomplish under the conditions of a modern chemical analysis service.

Within the Central Analytical Department of *Ciba-Geigy*, ICP-MS fulfils basically two different tasks: as a quick multi-element method it allows the rapid and sensitive determination of many trace elements which, so far, had to be determined successively by graphite-furnace AAS. When exceptionally low detection limits have to be obtained for one special element, ICP-MS is also used as a mono-element technique.

2. Experimental

The ICP-MS instrument used in our laboratory is the *VG PLASMAQUAD 1*. The instrument configuration and standard operating conditions are summarized in *Table 1*.

The standards used were either prepared from anal. grade reagents or from commercially available standard solns. The water used was *Millipore SQS*-water. The purification grade of all the acids was 'supra pure'.

3. Applications

3.1. Determination of Pt-Group Metals in Pharmaceuticals and Agrochemicals

Pt Group metals are frequently used as catalysts for hydrogenating reactions. Especially Ru, Rh, Pd, and Pt on activated charcoal or an inorganic carrier are used for the production of agrochemicals and pharmaceuticals. For some of these processes, severe catalyst losses were observed in our company. Because of the high costs of the catalyst metals, a series of analyses was done in order to investigate and control the causes for these losses.

In some cases, even ng/g amounts had to be determined in the raw products and in their mother-liquors. A suitable sample preparation for the mainly organic materials is the decomposition of *ca.* 50 mg of sample with 0.5 to 1 ml of a mixture HNO_3/HCl 2:1 in a sealed glass tube ('*Carius* digestion'). After the digestion, the concentrated acid mixture is diluted to 10 ml with doubly deionized H_2O. This results in a solution the ICP-MS can easily cope with. Calibration can usually be performed with an external standard. No internal standards or standard addition is needed. The limits of detection which can be obtained for Pt-group elements in aqueous solutions correspond to 2 to 10 ng/g in the solids.

As an example for the determination of Pt in a pharmaceutical raw product, *Fig. 1* shows the recorded mass spectrum in the

mass range of 190 to 199 amu (512 channels, 750 scan sweeps, 250 µs dwell time per channel). The Pt concentration was 52 ppb in this product. At such a concentration, even the Pt isotope pattern can be recognized. Compared to that, the spectrum obtained for a blank solution contains no Pt isotopes at all. Our investigations on the observed Pt losses have not been finished so far. At present, we know that the Pt concentrations are negligible in the raw products and the washing solutions.

3.2. Determination of Toxic Heavy Metals in Iron Oxides

This example describes the determination of Cd, Hg, Tl, and Pb in iron oxides. Such iron oxides are the by-products of different reduction processes. They are formed in vast amounts and are to be given to the cement industry for disposal. For that, the concentrations of some toxic heavy metals must not exceed the required limits.

Again, the digestion in a '*Carius* tube' is an appropriate sample preparation procedure. In the case of the mainly inorganic matrix, up to 100 mg are decomposed by 1.0 ml HNO_3/HCl 1:3. For the ICP-MS measurements, the concentrated solutions have to be diluted with doubly deionized H_2O, till their iron contents are below 1000 µg/ml. Y or In is used as an internal standard. Usually, the whole mass range is

Table 1. *Instrument Configuration and Standard Operating Conditions*

ICP-MS instrument	*VG PLASMAQUAD 1*
RF generator	*Henry*, 2.5 kW
ICP torch	*Fassel* type (*VG* standard)
Spray chamber	glass, watercooled to 10°C
Nebulizer	*de Galan V*-groove
Peristaltic pump	*ISMATEC MS-4* (8 rolls)
Sample cone	Ni, orifice 1 mm diameter
Skimmer	Ni, orifice 0.7 mm diameter
Incident power	1300 W
Reflected power	5–15 W
Coolant gas flow	12.5 l/min
Auxiliary gas flow	0.5–1.5 l/min
Nebulizer gas flow	0.67–0.72 l/min
Sample uptake rate	0.9–1.0 ml/min

Table 2. *Composition of Nutrient Solutions for Ecotoxicity Tests*

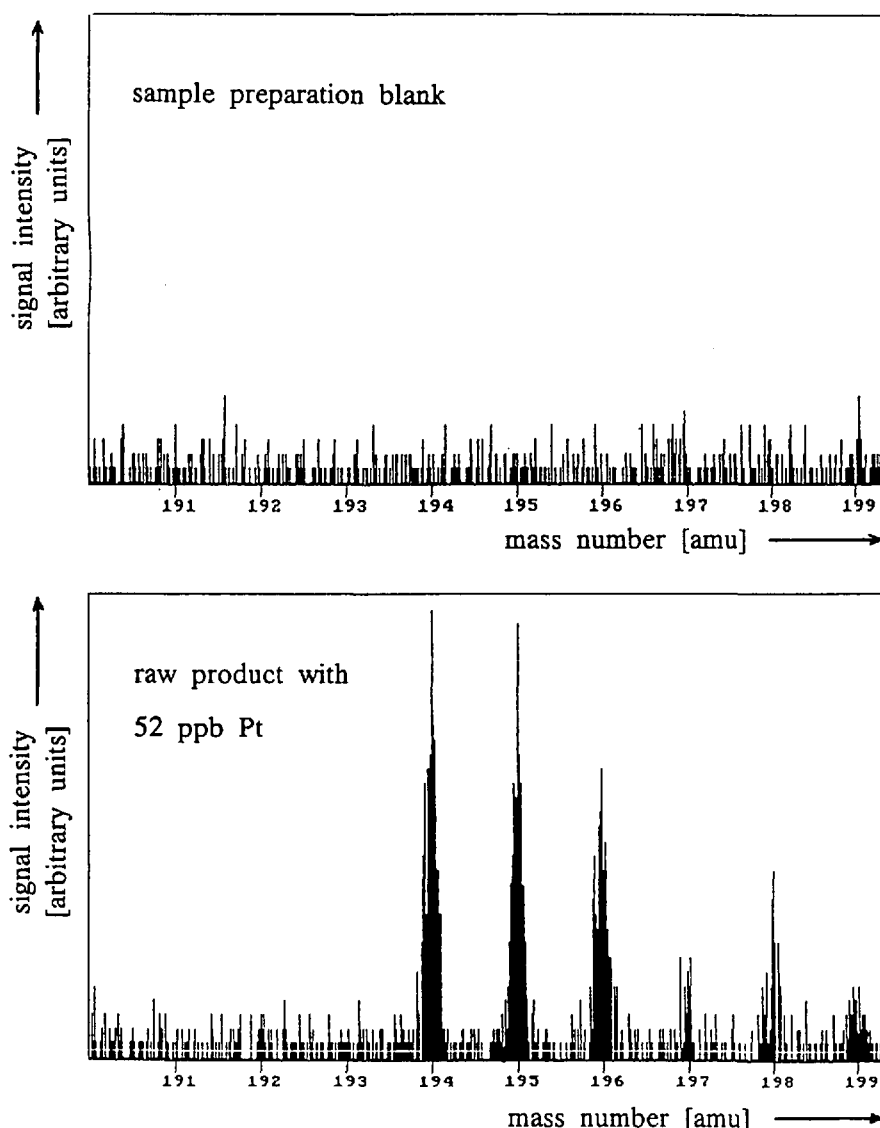|	Solution for algae [mg/l]	Solution for daphnia [mg/l]
$NaHCO_3$	50	65
NH_4Cl	15	
$MgCl_2 \cdot 6H_2O$	12	
$CaCl_2 \cdot 2H_2O$	18	294
$MgSO_4 \cdot 7H_2O$	15	123
KH_2PO_4	1.6	
$FeCl_3 \cdot 6H_2O$	0.08	
$Na_2EDTA \cdot 2H_2O$	0.1	
H_3BO_3	0.185	
$MnCl_2 \cdot 4H_2O$	0.415	
$ZnCl_2$	0.003	
$CoCl_2 \cdot 6H_2O$	0.0015	
$CuCl_2 \cdot 2H_2O$	0.00001	
$Na_2MoO_4 \cdot 2H_2O$	0.007	
KCl		6

Fig. 1. *Mass spectra for the determination of Pt in a pharmaceutical raw product.* Sample preparation: digestion with HCl/HNO₃ in a *Carius* tube; quantitation: external standard method.

recorded (5–239 amu, skipped mass regions: 11.5 to 22.0, 27.5 to 42.5, and 53.5 to 58.5 amu; 2048 channels, 250 scan sweeps, 250 μs dwell time per channel). Using this procedure, we can easily reach detection limits of 0.2 to 1 ppm for many elements. The concentrations in the sample for which a part of the spectrum is shown in *Fig. 2* were below 1 ppm for Hg and Tl as well as for Cd. The lead concentration was 1.7 ppm.
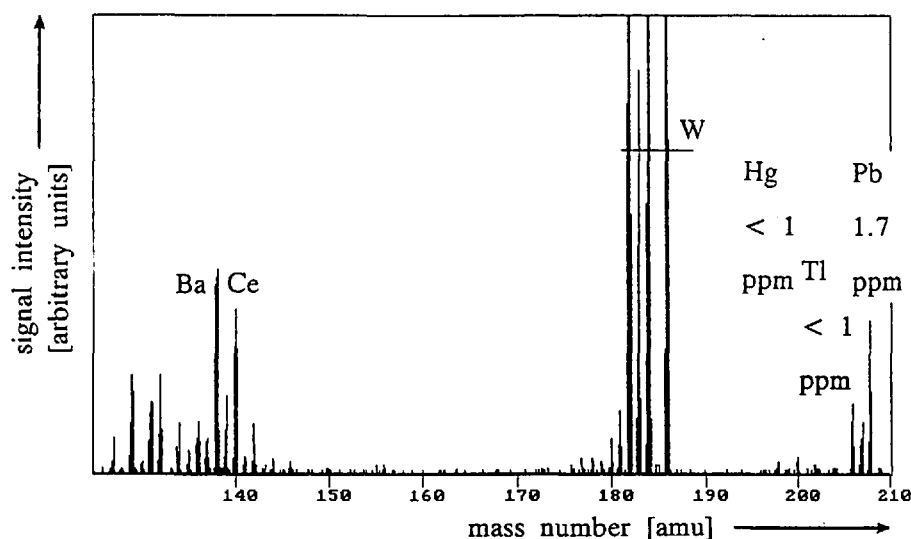

Fig. 2. *Mass spectrum of an iron oxide sample.* Sample preparation: digestion with HNO₃/HCl in a *Carius* tube; quantitation: internal standard method.

With the help of ICP-MS, we could also show that the Be and Cd concentrations, which had beforehand been measured by ICP-OES, were far too high. Obviously, in ICP-OES some of the numerous Fe lines had interfered with the analytical lines chosen for Be and Cd.

3.3. Determination of Sn in Nutrient Solutions

Many organotin compounds are known to be very toxic. In a series of ecotoxicity tests with algae and daphnia in their nutrient solutions (see *Table 2*), reliable results for Sn concentrations down to 0.05 ng/ml were demanded.

For measuring the solutions, no sample preparation, matrix removal, or preconcentration of the tin, is needed. For larger series, an internal standard (Y or In) has to be used for drift correction. As can be seen from the spectrum (mass range: 114–121 amu, 512 channels, 750 scan sweeps, 250 μs dwell time per channel) in *Fig. 3*, ICP-MS is capable of determining Sn concentrations of *ca.* 80 pg/ml without any problems. Even the characteristic isotope pattern of Sn is recognizable.

We had also tried to test these samples with graphite furnace AAS. However, we ran into serious problems with matrix effects with this method. Additionally, the detection limits were much worse.

3.4. Determination of Th and U in Semiconductor Materials

'Electronic chemicals' such as high-purity quartz as a filler material or polymer photo-resists for the protection of integrated devices are required to have extremely low levels of α-emitters. The photo-resists are sold in solutions containing *ca.* 40% of the solid. In these solutions, we have to specify concentrations of less than 0.1 ng/g for U and Th which are the two most important naturally occurring α-emitters. With the help of ICP-MS, we can even reach detection limits of 0.01 ng/g for those two elements. For that, the organic matrix is completely destroyed in a cool plasma asher. The use of a high-frequency-induced oxygen plasma for the ashing of organic samples has been described in detail by *Kaiser et al.* [2] and *Raptis et al.* [3]. As this digestion procedure is not so well-known, a schematic diagram of the system is given in *Fig. 4*.

For analysing the photo resists, *ca.* 2–3 g of a sample are weighed into a quartz digestion vessel. The digestion is performed at an RF power of 50 W. The O₂ flow rate is 3 l/h at the beginning and 1 l/h after half of the sample is digested.

When decomposition is complete the sample vessel is taken out of the plasma ashing device and inserted in a reflux heater. The residues are then dissolved by
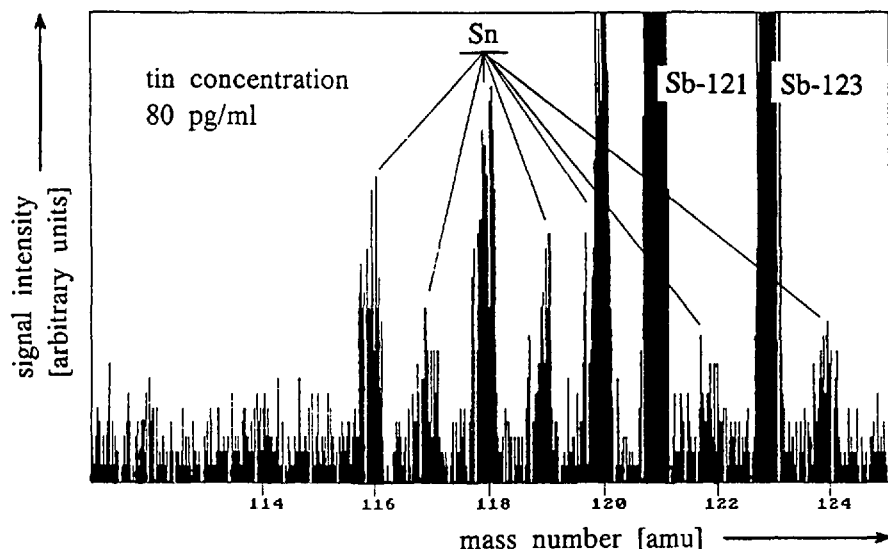
Fig. 3. *Mass spectrum of a nutrient solution containing tetraalkyltin compounds for ecotoxicity tests.* Total salt content: 110 mg/l, sample preparation: none; quantitation: external standard method.

Table 3. *U and Th Concentrations in Photo-resists*

Sample	U Concentration [ppt]	Th Concentration [ppt]
1	32	45
	34	46
	33 ± 1	45 ± 0.5
2	42	43
	40	53
	41 ± 1	48 ± 5
3	32	45
	34	46
	33 ± 1	45 ± 0.5
4	121	9
	117	21
	119 ± 2	15 ± 6
5	151	17
	135	14
	143 ± 8	16 ± 2

refluxing with 0.5 ml of 50% (v/v) HNO$_3$. For the measurements, the solution is diluted to 5 ml with doubly deionized H$_2$O.

Ashing the sample in the reactive oxygen plasma is practically free of contaminations. As the trace constituents of up to 3 g of sample material are dissolved in only 5 ml diluted acid, very low detection limits

can be achieved. *Table 3* summarizes the results of some photo-resist analyses. Since the U concentrations were close to the required limit in resists number 4 and 5, those materials were not processed.

Comparable detection limits as in the photo-resists can be achieved in high purity quartz after digesting it with HNO$_3$/

HF/H$_2$SO$_4$ mixtures. The digestion procedure and apparatus have been described in detail in [4]. This publication presents an overview on the development of a reliable procedure for the quality assurance of electronic-grade silicon dioxides using different analytical methods such as ICP-MS, XRF, OES, AAS, and NAA.

Fig. 5 shows the results of a quartz analysis. For the recording of these spectra, the peak hopping procedure was selected (3 points per peak, 10 DAC steps between points, 1000 μs dwell time per point, 2500 peak jump sweeps). Calibration was performed by means of the signal intensities of
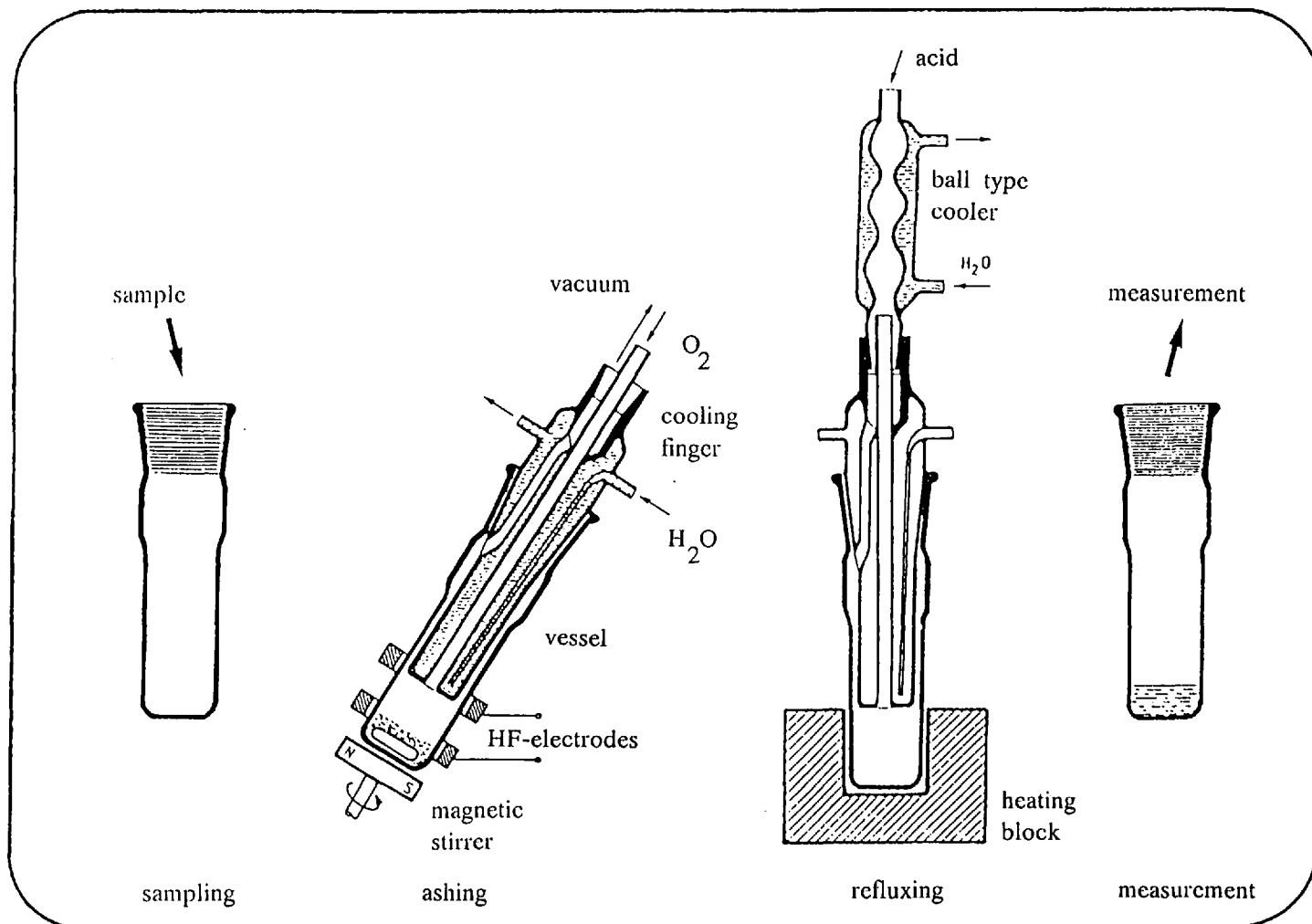

Fig. 4. *Cool plasma asher: operation scheme* (taken from [16])

Table 4. *Comparison of ICP-MS and INAA Results of U and Th Determinations in SiO₂ Samples*

Sample	U Concentration [µg/g]		Th Concentration [µg/g]	
	ICP-MS	INAA	ICP-MS	INAA
BCS-CRM 313/1	0.11	0.11	0.19	0.15
CERAC SiO₂ 99.9%, × 8653	0.67	0.60	0.97	0.91
DENKA FS-44	0.033	0.03	0.014	0.0140
CABOT CAB-O-SIL M-5	0.0002	< 0.0017	0.0002	0.0003

Table 5. *Data for the ⁸²Se Spike*

Concentration	2.44 µg/ml	
Isotope abundances	0.06%	⁷⁴Se
	0.53%	⁷⁶Se
	0.55%	⁷⁷Se
	1.76%	⁷⁸Se
	8.98%	⁸⁰Se
	88.07%	⁸²Se

the isotopes ^{232}Th and ^{238}U. The external standard method was used. The signal intensities which had been recorded for a sample with *ca.* 20 ppt Th and 127 ppt U clearly differ from those which had been obtained for the sample preparation blank and the background spectrum. The excellent agreement between the results obtained by ICP-MS and INAA (*Table 4*) clearly demonstrates the reliability of the sample treatment procedure and the ICP-MS measurements.

3.5. Determination of Se in Silver Nitrates: Comparison of Ar-ICP-MS and He-MIP-MS

Ag salts which are used for the preparation of photographic layers have to meet extremely high purity standards. Among other elements, Se has to be determined at concentrations as low as 100 ng/g. Because of its high ionization potential (9.75 eV [5]) and the interferences caused by molecular ions [6], Se cannot be detected so well by Ar-ICP-MS. The ionization degree is rather low in the Ar plasma, and the main isotopes are interfered by molecular ions such as Ar_2^+ and, in the presence of chlorine in the solution, $ArCl^+$. Consequently, the limit of detection in solutions for Se is comparatively poor. Additionally, in the case of the Ag salts analyses, the Ag matrix can cause severe matrix effects. At Ag concentrations above 1000 µg/ml, signal suppressions are observed. Hence, for reaching the required detection limits, a preconcentration of the Se or a matrix removal is inevitable. As with every separation step, one runs the risk of loosing a fraction of the element of interest, the only practicable way of doing these analyses, in our opinion, was the use of the mass spectrometric isotope dilution technique.

Principles of Mass Spectrometric Isotope Dilution Analysis (MS-IDA)

MS-IDA is known to provide very accurate and reliable analytical results [7–9]. Its principles are illustrated by the schematic mass spectrum of a Se determination in *Fig. 6*. An accurately known quantity of a spike is added to the sample. This spike must contain the element of interest in an isotopic composition other than that in the sample. The element to be determined, therefore, has to posses at least two stable or long-lived radioactive isotopes. Enriched ^{82}Se is used in the example shown in *Fig. 6*. After the addition of the spike, the spike and the sample isotopes must be mixed completely. This implies that a solid sample must be chemically decomposed. The resulting isotope ratio is then measured in a mass spectrometer. In the example of the Se determination, the ratio ^{77}Se/^{82}Se is measured. As can be seen in *Fig. 6*, the ion intensities of the lighter (^{77}Se) and heavier (^{82}Se) isotopes in the mass spectrum are identical to the sum of the sample portion and the spike portion. Hence, *Eqn. 1* follows for the isotope ratio R:

$$R = (N_S h_S^{77} + N_{Sp} h_{Sp}^{77})/(N_S h_S^{82} + N_{Sp} h_{Sp}^{82}) \qquad (1)$$

where N is the number of atoms, h the isotope abundance [%], and subscripts S and Sp indicate sample and spike, respectively. One can now solve *Eqn. 1* and calculate the amount of element in the sample with the help of the measured isotope ratio R, the known isotopic composition of the element in the sample and in the spike, and the amount of spike added to the sample. MS-IDA is, thus, a definitive method, since it requires no external calibration.

Moreover, after the mixing of spike and sample isotopes, the quantitative isolation of the element of interest is unnecessary. Substance losses during chemical sample treatment procedures or during the isolation of an element by extraction or precipitation reactions have, therefore, no influence on the accuracy of the analytical results.
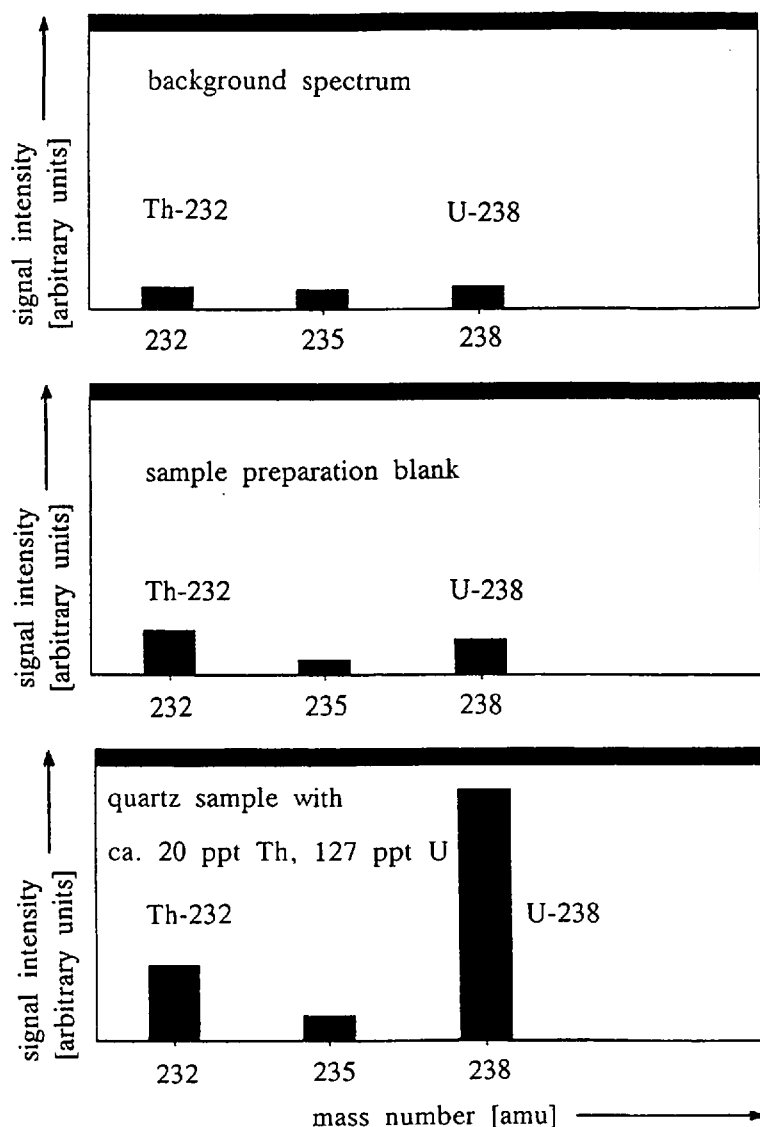
Fig. 5. *Mass spectra for the determination of U and Th in high purity quartz.* Sample preparation: digestion with HF/HNO₃/H₂SO₄, quantitation: external standard method or isotope dilution analysis.
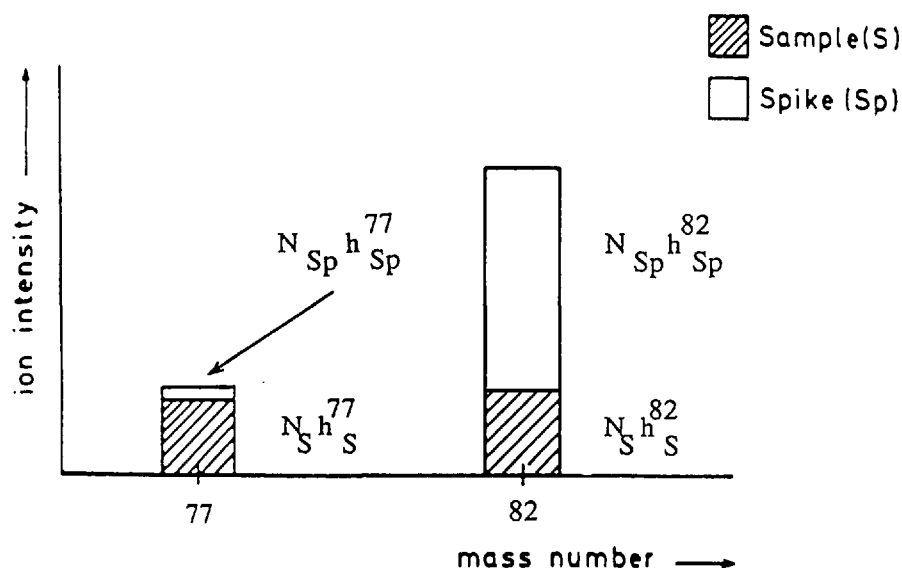
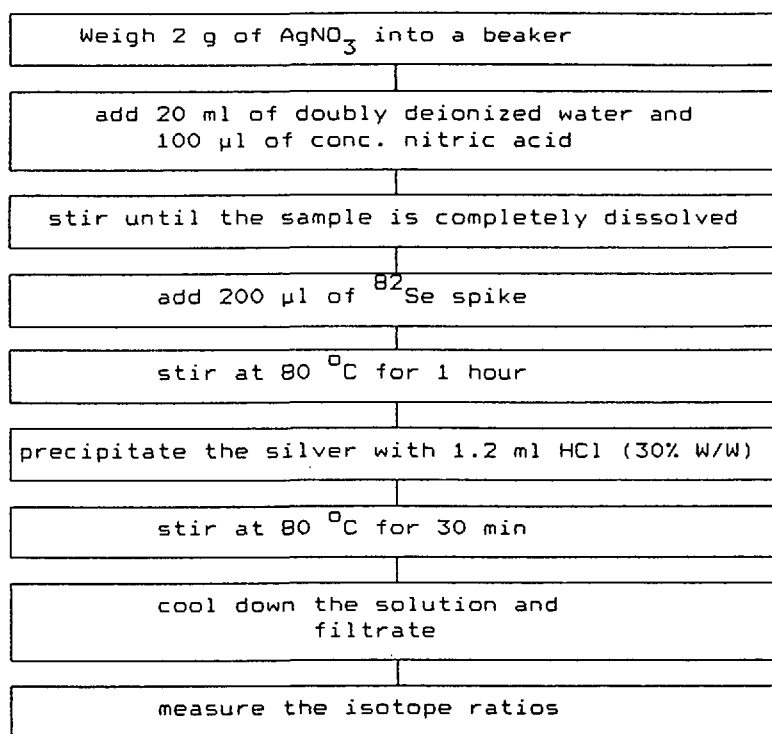Fig. 6. *The principle of MS-IDA by the schematic mass spectrum of Se*

Fig. 7. *Sample preparation scheme for the determination of Se in silver nitrates*

Table 6. *Ar-ICP vs. He-MIP: Comparison of Some Physical Properties*

			Ar-ICP	He-MIP
Thermal conductivity	[W/min·K]	[14]	0.017	0.149
Heat capacity	[J/kg·K]	[14]	523	5188
Thermodynamic temp.	[K]	[15]	5000	2500
Gas flow through sampler (1.14 mm diameter)	[l/min]	[15]	2.5	13
Ionization potential of the plasma gas	[eV]	[5]	15.8	24.9

Table 7. *Determination of Se in Silver Nitrates by MS-IDA: Isotope Ratios*

Sample	Ar-ICP-MS	He-MIP-MS	
	$^{77}Se/^{82}Se$	$^{77}Se/^{82}Se$	$^{80}Se/^{82}Se$
Blank	0.008 ± 0.004	0.013 ± 0.008	0.10 ± 0.04
1	0.018 ± 0.005	0.025 ± 0.004	0.147 ± 0.009
	0.012 ± 0.003		
2	0.034 ± 0.011	0.047 ± 0.002	0.31 ± 0.02
	0.043 ± 0.006		
3	0.34 ± 0.01	0.37 ± 0.02	2.40 ± 0.04
	0.33 ± 0.03		
4	0.034 ± 0.003	0.045 ± 0.008	0.31 ± 0.03
	0.048 ± 0.008		

Se Determinations with MS-IDA

For our analyses, we used a spike which was enriched in ^{82}Se. The data of this spike are summarized in *Table 5*. For the isotope ratio measurements with Ar-ICP-MS, the isotopes ^{77}Se and ^{82}Se were selected. The mass range between 73 and 84 amu was recorded (512 channels, 750 scan sweeps, 250 µs dwell time per channel). The Se species, which are of interest to us, are soluble in mineral acids or perform an isotope exchange. Ag can be precipitated nearly quantitatively as silver halide, thus, enabling an easy matrix separation.

The sample preparation scheme is summarized in *Fig. 7. Ca.* 2 g of $AgNO_3$ are dissolved in 20 ml of 0.5% (v/v) HNO_3. After the addition of 0.5 µg of Se spike, the solution is heated to 80° and stirred for 1 h. Then, Ag is precipitated with conc. HCl (*s.p.*) using 0.60 ml of HCl per 1 g of $AgNO_3$. Stirring is continued for 30 min. After cooling down, the solution is filtrated. In the filtrates, the isotope ratio measurements are performed.

The most important part of this sample preparation scheme is the exact measuring out of the amount of HCl added. A small excess of HCl gives raise to a strong interference of $^{40}Ar^{37}Cl^+$ on $^{77}Se^+$, whereas a deficiency results in too high a Ag concentration in the solution. Its consequences are not only the already mentioned signal suppressions but also an enormous memory effect. Small interferences, however, can be corrected *via* the signal intensity at m/z 75 ($^{40}Ar^{35}Cl^+$) and the known isotope ratio $^{35}Cl/^{37}Cl$. For that, of course, no As must be contained in the solution. The use of HBr or HI for precipitating Ag does not cure these problems, because those acids also contain chlorine. In any case, AgCl, being more soluble than AgBr and AgI, remains in solution.

Se Determinations with He-MIP-MS

The problems of the $ArCl^+$ and Ar_2^+ interferences on the Se isotopes should possibly be overcome with the use of He as a plasma gas. *Table 6* briefly summarizes the basic differences of the Ar and the He plasma. The He plasma has a lower thermodynamic temperature, a better thermal conductivity, and a much higher ionization potential than the Ar plasma. Especially the low thermodynamic temperatures and the good thermal conductivity cause the He plasma to be rather unstable against solvent loading. Despite these problems, *VG Instruments* together with Prof. *Caruso* and coworkers at Cincinnati University have developed a He-MIP (Microwave Induced Plasma) as an ionization source for a quadrupole mass spectrometer [10–13]. This system is commercially available now and we were given the possibility to measure some isotope-diluted samples. The samples were prepared the same way, as illustrated in *Fig. 7*. The isotope ratio mea-
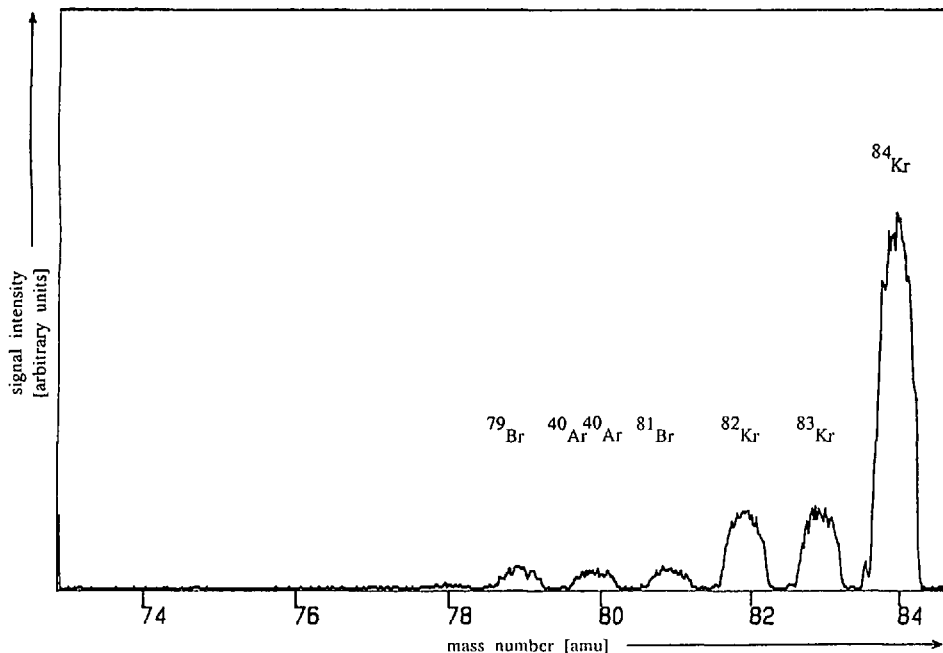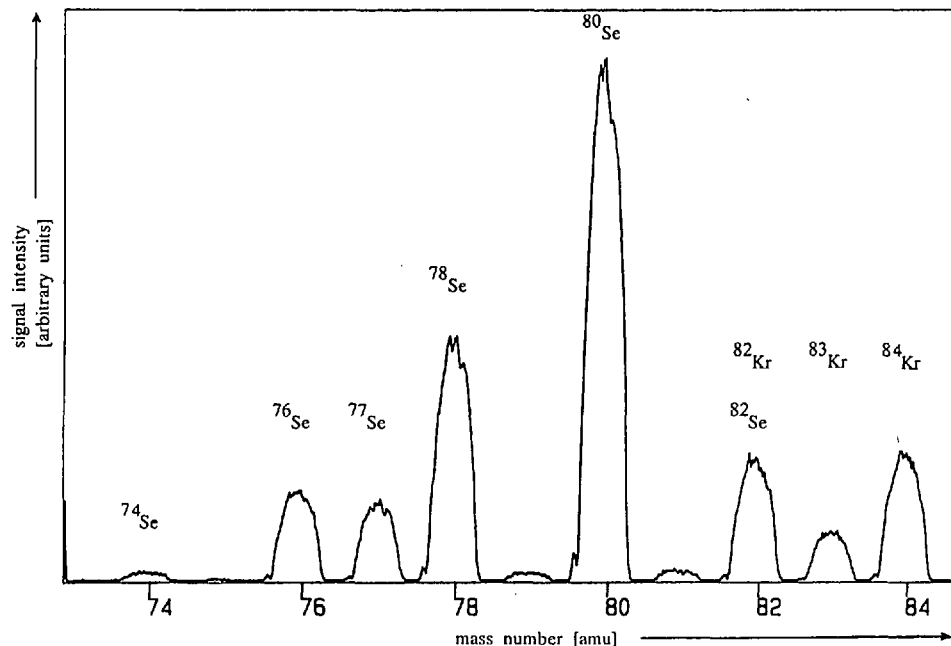
Fig. 8. *Mass spectrum of a 1% (v/v) HNO₃ blank*

Fig. 9. *Mass spectrum of a Se standard solution* (200 ng Se/ml in 1% (v/v) HNO₃)

surements were performed at Cincinnati University.

The spectra in *Figs. 8* and *9* clearly show the advantages of the He-MIP-MS: the background spectrum (*Fig. 8*) collected with a 1% HNO₃ solution is nearly entirely free of Ar_2^+ interferences. Only a small peak at m/z 80 is registered. The spectrum also displays the isotope pattern of Kr which is contained as an impurity in the He. $^{82}Kr^+$ interferes with $^{82}Se^+$, but this interference can be corrected *via* the isotope ratio $^{82}Kr/^{83}Kr$. *Fig. 9* shows the spectrum

of a Se standard at a concentration of 200 ng Se/ml. Because of the small background level at m/z 80, the ratio $^{80}Se/^{82}Se$ can be used for the isotope dilution calculations.

Tables 7 and *8* summarize some analytical results. The isotope ratios as well as the concentrations agree very well for the AgNO₃ samples and for the blanks. As far as the Ar-ICP-MS is concerned, the results of two independent measurements are listed. For the He-MIP-MS, the reproducibility of the $^{80}Se/^{82}Se$ measurements is much better than that of the $^{77}Se/^{82}Se$ mea-

surements. Using the $^{77}Se/^{82}Se$ ratios, a blank value different from zero is calculated. This might be caused by an unsufficiently corrected interference from $^{40}Ar^{37}Cl^+$. The results for sample 1 are quite close to the detection limit in the case of the Ar-ICP-MS. Nevertheless, the agreement with the results obtained with the He-MIP-MS is still acceptable. All in all, sample preparation is much easier for He-MIP-MS, because the main interference problems can be overcome.

4. Conclusions

Today, ICP-MS can be regarded to be one of the most powerful, sensitive, and selective methods for the ultra-trace level determination of elements. So far as the Central Analytical Department of *Ciba-Geigy* is concerned, the analytical problems discussed in this paper could not have been solved without the use of this method. Preliminary results obtained with a He-MIP-MS are very promising. For some special applications, the He plasma can be expected to even improve the performance of plasma-source mass sprectrometry.

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