On the use of inductively coupled plasma mass spectrometry as an element specific detector for liquid chromatography: optimization of an industrial tellurium removal process

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Abstract

The current status of inductively coupled plasma mass spectrometry (ICP-MS) can be defined as a versatile element and isotope specific detection technique of high sensitivity and wide element coverage. In conjunction with this type of detector a variety of sample introduction systems is used enabling the introduction of samples in liquid, solid and gaseous form. In addition, ICP-MS instruments are increasingly being used in speciation studies especially as a detector for liquid chromatography (LC). This is demonstrated by the following representative application. A considerable part of the industrial chemicals currently produced by DSM is derived from an (amm)oxidation process on the basis of sophisticated heterogeneous catalysts in which tellurium plays an important role. A drawback of tellurium is its volatility resulting in material losses and a corresponding decay in catalytic properties. These tellurium losses show up in waste water drained at a concentration of 0.5–1.5 mg Te/l. Supply of this waste water to a central waste water purification plant leads to biological methylation of tellurium into dimethyltelluride $Te(CH_3)_2$ with an unpleasant garlic smell. Therefore a tellurium removal process was developed based on the cementation of tellurium onto iron. This process showed unacceptably low removal efficiencies when supplied with freshly drained waste water. LC–ICP-MS experiments revealed the occurrence of tellurium compounds that were only slowly converted into tellurite and tellurate. Conversion parameters and conditions were extensively studied by LC–ICP-MS experiments. Process conditions developed on a benchscale were successfully applied in a plantscale tellurium removal process. This process is capable of removing tellurium from a continuous 100 m^3/h waste water supply to a concentration level of 0.01–0.03 mg Te/l. © 1998 Elsevier Science B.V.

Keywords: Mass spectrometry; Inductively coupled plasma mass spectrometry; Detection, LC; Tellurium

1. Introduction

Since the commercial introduction of inductively coupled plasma mass spectrometry (ICP-MS), the technique has found widespread application in the various fields of inorganic elemental analysis. The versatility, robustness and matrix tolerance of ICP-MS has been shown in numerous publications and applications and are also reflected by the variety of front-end analytical arrangements and sample introduction systems that are used in combination with an ICP-MS instrument. As a consequence, it is more appropriate to consider an ICP-MS instrument as an element (or isotope) specific detector, in front of which a set-up is installed suited for the analytical task that has to be fulfilled. It is no surprise then, that ICP-MS is increasingly being used for elemental speciation studies and that almost the complete chromatographic "toolbox" has been used in conjunction with ICP-MS instruments.
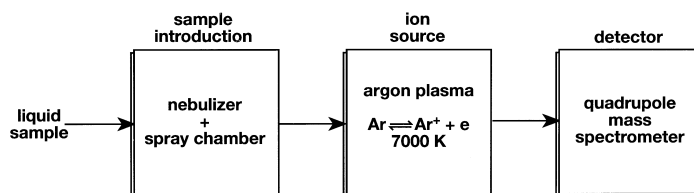
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Fig. 1. Block diagram of an ICP-MS instrument.

This article is dedicated to liquid chromatography (LC)–ICP-MS and is subdivided into two parts. The first part deals with the more general, instrument and technique related aspects of LC–ICP-MS. In the second part of this article a representative practical application of this hyphenated technique is described.

2. ICP-MS instrumentation

In Fig. 1, the outline of an ICP-MS instrument is presented as a block diagram consisting of the sample introduction system, the inductively coupled argon plasma (ICP) and the mass specific detector. In subsequent sections, special attention is paid to the unfamiliar aspects of instrumentation and technique i.e., the use of an argon plasma as an ion source and the sampling of ions. Finally, the analytical potentialities of the combination LC and ICP-MS are demonstrated by means of the optimization of an industrial tellurium removal process.

2.1. ICP as an ion source

Already in an early stage of the development of ICPs as an excitation source for atomic emission spectroscopy (AES), it was recognized that its characteristics made it suitable as an ionization source for inorganic MS. Basically, an ICP is an electrodeless discharge created in a continuous stream of argon. An ICP operates at atmospheric pressure and is sustained by energy generated in a radio frequency (RF) generator. RF energy of typically 1.25 kW at 27.12 MHz is coupled to the plasma by means of a cooled 3-turn coil. The coil can be considered as the primary of a transformer wherein the plasma acts as the secondary. The plasma is maintained inside an arrangement of three open

concentric quartz tubes, better known as the plasma torch. The plasma torches used today are almost exclusively based on the original Fassel design [1]. The Fassel torch used in the Elan 500 ICP-MS, is depicted in Fig. 2. In this type of torch, annular regions are supplied with argon by tangentially placed side tubes, usually 12–15 l/min for the outer region (called coolant gas) and 0–2 l/min for the
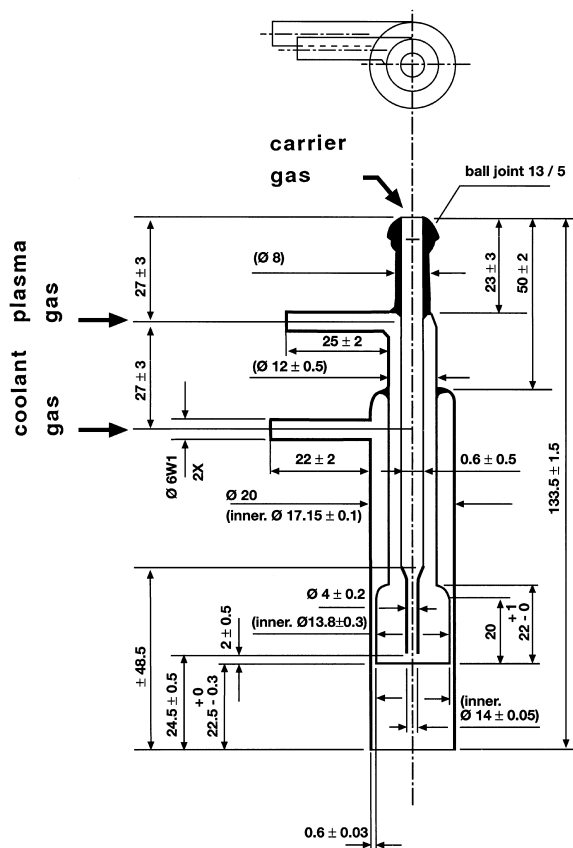

Fig. 2. Detailed drawing of the Fassel torch used in the Elan 500 ICP-MS instrument. The dimensions given are all in mm (from P&H Glass Technology, with permission).

inner region (called plasma gas). In this way a laminar flow and a toroidal ICP is created. The ICP torch must be considered as one of the most critical components of an ICP-MS instrument so that highest demands are set with respect to accuracy and precision of dimensions and annular spacings. Fundamental studies concerning the characteristics and properties of ICPs have been published by Boumans [2] and Montaser and Golightly [3].

Nowadays, a large variety of sample introduction systems are used with ICP-MS. Nevertheless, by far the most common applied means of sample introduction is pneumatic nebulization. In a pneumatic nebulizer, a stream of argon expanding with high velocity from an orifice converts a stream of liquid into an aerosol of droplets with a wide spread in diameter. Pneumatic nebulizers are almost exclusively used in conjunction with a spray chamber that serves as a droplet separator, allowing droplets with diameters of typically <10 μm to pass and enter the ICP, while the remainder is removed and delivered to waste. A (very) often used combination for ICP-MS sample introduction is the so-called Meinhard nebulizer incorporated in a Scott type double pass spray chamber. Liquid consumption of this type of nebulizer is typically 1–3 ml/min at an argon flow-rate of 1 l/min. Of the aerosol produced accordingly only 1–2% exhibits a droplet diameter able to survive the spray chamber and consequently enters the ICP. When the aerosol expands from the carrier tube (inner diameter=1.4 mm) its linear velocity becomes 10.8 m/s. Consequently, a hole is "punched" into the plasma that is mostly referred to as the central or axial channel. The sample material introduced accordingly is exposed to the hostile conditions of the ICP (5000–9000 K) and is successively desolvated, vaporized and dissociated, whereafter the atoms are ionized. The dwell time in the ICP equals a few milliseconds. Most elements are ionized to a large extent (>95%), especially those with first degree ionization potentials below 8–9 eV [4], thus making the ICP a very effective ion source for inorganic MS.

2.2. Ion sampling

Fig. 3 shows an ICP-MS interface in schematic form, sampling an argon plasma. Sampling ions from an ICP and transporting the ion beam into a mass
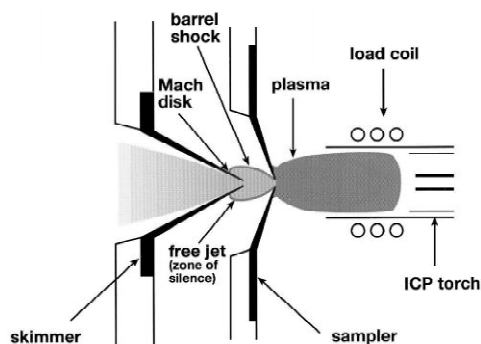

Fig. 3. Schematic diagram of an ICP-MS interface, during ion sampling.

spectrometer means converting conditions from the atmospheric pressure and high temperature of the ICP ion source into the high vacuum and room temperature conditions of the mass spectrometer, preferably without changing the composition of the "sample". It is beyond doubt, that the interface between ICP and mass spectrometer is a key part of an ICP-MS instrument and of crucial importance to its analytical performance. The differentially pumped interface design depicted in Fig. 3 originates from molecular beam techniques and has been adapted for ICP ion sampling [5–9]. To obtain the highest ion yield, the central interface axis is adjusted to the central torch axis. Part of the plasma is extracted through the sampler orifice (diameter 0.040–0.045 in.; 1 in.=2.54 cm) into the first vacuum region, which is evacuated by means of mechanical pump to a residual pressure of typically 600–800 Pa. The sampled gas expands in this first vacuum region with a rapid decrease of density and temperature. In the meantime, the flow speed accelerates very fast exceeding the speed of sound, forming a free jet. As the gas is transported further downstream of the sampler orifice, the flow speed reaches a maximum and decreases again until the local speed of sound is attained. At this position, the gas of the free jet collides with the background gas and reheats again to over 2000 K [10]. Consequently, the free jet is bounded by the concentric barrel shock and perpendicular Mach disk shock waves (see Fig. 3). The region within this shock structure is used for the skimming process.

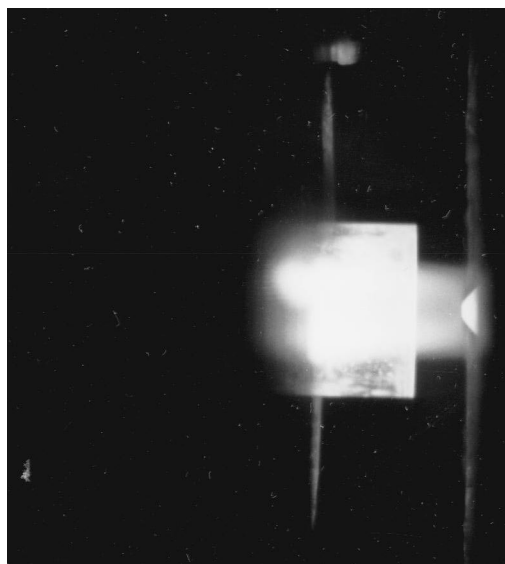Calculations have shown, that the skimmer orifice

Fig. 4. View on the argon plasma in front of the sampler, in the Elan 500 ICP-MS instrument.

(diameter 0.030–0.035 inch) has to be at a distance <0.7×Mach disk distance, in order to avoid contributions from the surrounding background gas. In the Elan system, the skimmer orifice is located at a distance of 6.1 mm downstream of the sampler orifice which is well within the free jet region. Fig. 4 shows a plasma in operation while ions are extracted by means of the immersed sampler located at the right.

Downstream of the skimmer, ions have to be transmitted to the quadrupole mass analyzer while

separating them from neutral species. This is accomplished by focusing the ions into a narrow, collimated beam whilst allowing all other species to be deflected and pumped away. In addition, the kinetic energy distribution of the transmitted ions must be narrowed in order to obtain the best spectral characteristics of the quadrupole mass analyzer. This is accomplished by means of an ion optic arrangement.

2.3. ICP-MS as a detector for LC

A schematic diagram of an Elan 500 ICP-MS instrument is presented in Fig. 5. Essentially, coupling of an LC instrument to an ICP-MS instrument is straightforward and can be accomplished by simply connecting the outlet of an LC column with the liquid inlet of a pneumatic nebulizer. Preferably, the dead volume of such a connection is kept as small as possible. The point is that the resolution gained by the LC separation must not be (substantially) degraded by the dead volumes introduced by nebulizer and spray chamber. In general, peak broadening effects resulting from the use of nebulizer and spray chamber have been reported as being acceptable [11,12] so that in most cases no attempt is made to optimize spray chamber design [13], mobile phase flow-rate or spray chamber placement [14]. On the other hand, the LC resolution obtained can be maintained by using a so-called direct injection nebulizer (DIN) which operates without spray chamber and at low liquid flow-rates (10–100 μl/ min). By means of a liquid split, an adequate part of
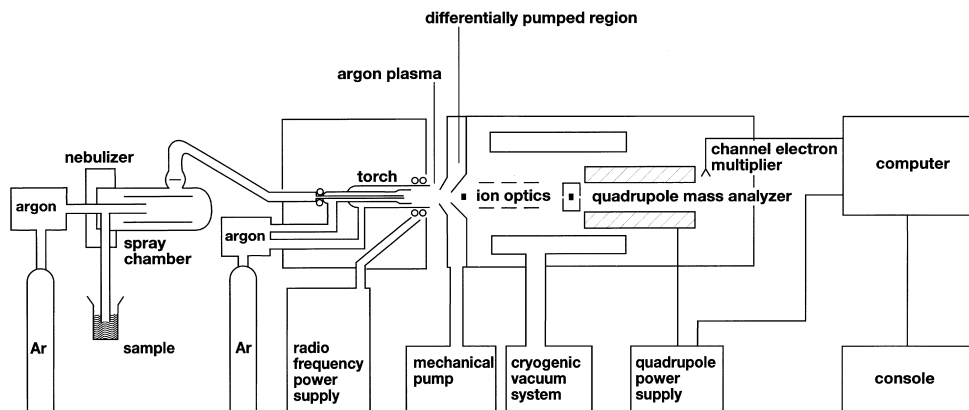

Fig. 5. Schematic diagram of an Elan 500 ICP-MS instrument (from Perkin-Elmer Sciex, with permission).

the eluate is introduced into the DIN and subsequently completely nebulized into the ICP.

The major analytical advantages of an inductively coupled argon plasma ion source are its matrix tolerance and its ability to convert the material introduced predominantly into single charged atoms (M^+). Consequently, an ICP-MS instrument exhibits (principally) uniform sensitivity for an element, irrespective of the compound(s) the element originates from. Both aqueous and organic solutions can be handled fairly easily by an appropriate combination of liquid flow-rate, spray chamber temperature and the RF power to sustain the plasma and isocratic as well as complex gradient LC techniques can be employed. In principle, there is no limitation on the use of (organic) solvents as long as the ICP ion source is kept operating and does not extinguish. The use of organic solvents however, can lead to depositions of elementary carbon at the sampler and skimmer aperture resulting in unstable and irreproducible ICP-MS operation. By the addition of oxygen (typically 0.02–0.05 l/min) to the nebulizer argon, this problem is circumvented.

Once ionized in the argon plasma and sampled by sampler and skimmer, the ion beam is analyzed by means of a quadrupole mass analyzer and consequently, full benefit can be taken from its use. This can be summarized as wide element coverage, simple spectra, wide linear dynamic range, low detection limits, multielement character as a result of a high change over speed between elements (isotopes) and the ability to determine isotope ratios. Interpretation of chromatograms can be carried out both qualitatively and quantitatively. Finally, the use of LC–ICP-MS is described in several excellent reviews [15–22].

2.4. Analytical drawbacks

The interferences occurring during ICP-MS analysis, can roughly be subdivided in spectral and matrix interference.

An interference is characterized as a spectral interference, when partial or complete overlap occurs with the analyte isotope peak and consequently, the net analyte signal cannot be isolated from the interferent. The spectral interferences occurring in ICP-MS can have the following origin: (1) isobaric overlap by concomitant elements; (2) overlap caused by polyatomic ions induces by sample matrix, solvent and the plasma element(s); (3) overlap caused by doubly charged (M^{2+}) and oxide ions (MO^+).

Isobaric interferences generally do not pose a serious problem, because in most cases a noninterfered isotope is available or an interelement correction can be carried out. Inherently, low abundant isotopes have to be used resulting in decreased sensitivity and degraded detection limits.

Polyatomic ions have the general form $(M_x)_n^+$, wherein M_x represents the constituent isotope(s) and n the number of isotopes per polyatomic species. A polyatomic ion can be composed of all isotopes present or added to the argon plasma. The more constituent isotopes per polyatomic species, the lower the probability that they really show up during ICP-MS analysis. Therefore, the maximum number of constituent isotopes is generally set at three. Some typical examples of polyatomic interferences are: (i) $^{40}Ar^{35}Cl^+$ and the mono-isotopic $^{75}As^+$; (ii) $^{12}C^{12}C^+$, $^{12}C^{13}C^+$, $^{13}C^{13}C^+$ and all Mg isotopes; $^{24}Mg^+$, $^{25}Mg^+$, $^{26}Mg^+$; (iii) $^{23}Na^{16}O^{16}O^+$ and the mono-isotopic $^{55}Mn^+$; (iv) $^{31}P^{14}N^{14}N^+$ and the mono-isotopic $^{59}Co^+$.

In principle, MO^+ ions have to be classified also as a polyatomic interference. However, since MO^+ is traditionally used as an instrumental parameter that has to be minimized (which also applies for M^{2+}), it is always dealt with separately. The occurrence of both species is strongly influenced by instrumental parameters such as ICP forward power, spray chamber temperature, nebulizer gas flow and the Z-coordinate, i.e., the part of the plasma that is being sampled.

In general, polyatomic spectral interferences pose the most serious problem in quadrupole-ICP-MS analysis, not only because detection limits are degraded but the measured intensity is or can be attributed to the analyte ion instead of partly or even completely to the interfering ion(s). It should be noted however, that polyatomic spectral interferences mainly occur in the region below mass 100.

It is generally accepted, that ICP-MS is more susceptible to nonspectroscopic matrix interferences than its mature sister inductively coupled plasma atomic emission spectrometry (ICP-AES). These matrix interferences become perceptible by suppres-

sion and (sometimes) enhancement of the analyte signal. Since both techniques use the same (or equivalent) sample introduction systems and argon plasmas, it is reasonable to assume that, as far as these parts are concerned, interferences are comparable. The difference in behaviour occurs hereafter, i.e., in the detection system used. By the use of classical atomic spectrometry analytical techniques such as matrix matched standards, standard addition and internal standards, accurate and precise analytical results are achieved. The most accurate results however, will be obtained by isotope dilution (ID) ICP-MS.

3. Tellurium containing catalysts

The majority of the primary chemicals currently produced is derived from petroleum and natural gas resources. The processes applied are made selective by the use of catalysts that lower the activation energy or provide a facile reaction path towards the desired product.

Of great industrial importance is selective (amm)-oxidation by heterogeneous catalysis. The most widely used (amm)oxidation catalysts are mixed metal molybdates or antimonates, often containing tellurium in various concentrations [23–26]. Usually, the composition of these catalysts is very complex and in their formulations tellurium operates either as a promoter or as a structural component [27,28]. Typical examples are the oxide systems (Fe, Te, Mo)O [29], (Fe, Se, Te)O [30], (Ce, Mo, Te)O [31,32] and others. The variety of valence possibilities of tellurium is an important asset of this element. Whereas the oxidation states of tellurium are likely to be relevant to the stability of the catalyst system, they certainly also influence the individual roles of the other elements present.

In industrial practice, the lifetime of a catalyst is crucial. A drawback of tellurium is its volatility resulting in material losses and as a consequence a corresponding decay in catalytic properties. Use of tellurium containing catalysts in the liquid phase is generally without a volatility problem. However, volatilization losses do occur in the vapor phase. A

combination of approaches is generally used to maintain adequate catalytic properties. In this respect an elegant but quite difficult approach is the inter-catalyst redox stabilization through the presence of powerful reoxidation elements such as Ce, V, Cu, Fe and U [33]. In spite of this, tellurium losses cannot be avoided completely and are often compensated by intermittent or continuous addition of tellurium to the reactor.

As an important producer of organic chemicals DSM has considered the plantscale introduction of catalytic tellurium, while paying attention to the unavoidable traces of tellurium in waste water streams. Complete substitution of running catalysts by tellurium containing catalysts would result in a total waste water volume of 100 m^3/h with an (estimated) concentration of 0.5–1.5 mg Te/l. All DSM waste water is collected and eventually biologically purified in a purification plant (IAZI) with a capacity of 4000 m^3/h.

In an early stage of the catalyst evaluation process, the influence of tellurium containing waste water on the water purification process was investigated in a benchscale IAZI. It was noticed that through the addition of tellurium containing waste water an unpleasant garlic smell was generated. Through an intermittent supply of tellurium to the benchscale IAZI whilst carrying out odour tests, the occurrence of the garlic smell could be assigned to a Te compound. In addition, the Te concentration added was varied and could be related to the magnitude of the garlic smell. By studying the relevant literature [34–36] the conclusion came forward that the Te compound had to be $Te(CH_3)_2$.

In compliance with our environmental responsibility, plantscale introduction of tellurium containing catalysts could only be tolerated by removal of tellurium from the waste water before entering the purification process. Consequently, a research program was initiated to remove tellurium from a total volume of up to 150 m^3/h containing 0.5–1.5 mg Te/l in the presence of 5–15 g/l of organics comprised of an estimated 200 different compounds.

This article describes the insights that have been gained by studying the removal process by means of ICP-MS and LC–ICP-MS experiments. These experiments have proven to be a substantial contribu-

tion to the reliable and reproducible operation of the tellurium removal process during the past years.

4. Experimental

4.1. Tellurium removal

Extensive experiments carried out with the bench-scale IAZI showed, that at a concentration of approximately 1 μg Te/l in the IAZI water no tellurium could be detected in the surrounding air. These measurements were performed both by odour determinations according to the recommendations made in Ref. [37] and by graphite furnace atomic absorption spectrometry (GFAAS) in various washing liquids after injection of large volumes of surrounding air. A concentration of 1 μg Te/l in the IAZI water corresponds to 0.02–0.04 mg Te/l in the waste water drained from the (amm)oxidation processes.

A variety of options for tellurium removal were studied or experimentally verified. Cementation of tellurium onto iron according to:

$$Te^{6+} \quad Fe^{2+} \quad Te^{0}$$
$$Fe^{3+} \quad Te^{4+} \quad Fe^{0}$$
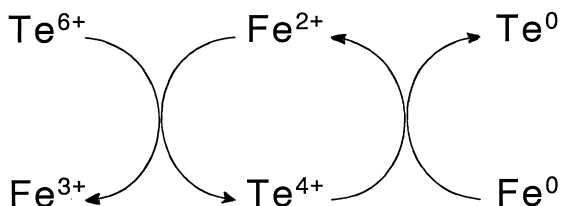
was finally selected whereby the hexavalent tellurium is first reduced to Te^{4+} as a result of the oxidation of Fe^{2+}. Cementation of tellurium is widely applied in metal refinement processes [38]. Despite its widespread use, only one study deals with the recovery of Te (and Se) from industrial waste waters [39]. Invariably however, all studies refer to cementation (by Zn, Fe, Al and Cu) of relatively high Te concentrations (g/l). Since the cementation reagent is dissolved in proportion to the tellurium concentration, it is obvious that from an environmental point of view, iron was the best choice.

A benchscale tellurium removal process was developed capable of purifying the waste water in a continuous mode to a concentration of well below 0.05 mg Te/l. To accomplish this, the pH of the waste water (normally pH 3–4) was adjusted to pH 10 ± 0.1 (NaOH addition) being the optimum pH for tellurium cementation. Next, the waste water was filtered and supplied to cementation columns having a residence time t_{res} of 1 h filled with iron. In practice, only once a week sufficient freshly drained waste water was collected to serve as the starting material for the week to come. The total volume of waste water was adjusted to pH 10 and connected to the cementation columns. Therefore, the residence time at pH 10, before being supplied to a retaining column, varied between 0–7 days.

On evaluating the experimental results over an extended period of time it was noticed that freshly drained waste water adjusted to pH 10 showed inferior removal efficiencies than water kept at pH 10 during several days. The possible influence of "aging" was tested by continuously supplying freshly drained waste water to several of the experimental cementation columns while adjusted to pH 10 just before supply to the columns. This procedure did lead to low (25–50%) and irreproducible tellurium removal efficiencies hereby indicating the possible occurrence of different Te compound(s) that were successfully converted into Te^{4+} and Te^{6+} as a result of prolonged NaOH exposure. Therefore, separation by means of LC–ICP-MS was chosen to provide insight in the problems encountered.

4.2. Analytical instrumentation

4.2.1. MS

The ICP-MS instrument used for this work is a Perkin-Elmer Sciex Elan 500 equipped with a Gilson minipuls II peristaltic pump and an IBM PS/2 Model 70 computer using the Version 2.01 Elan 5000 software. The instrument was equipped with a cooled Scott-type double-pass spray chamber and a Meinhard TR-30-A3 nebulizer incorporated in a PTFE end-cap. The torch used was a Sciex "short" torch. All argon flow-rates were mass flow controlled (Brooks Model 5850 C, Emerson Electric, Hatfield, PA, USA). Platinum samplers and skimmers were used throughout. The ICP-MS operating and analysis conditions are summarized in Tables 1 and 2, respectively.

Table 1
ICP-MS operating conditions

Sample introduction	
Spray chamber	DSM organic, temp. 1°C
Nebulizer	Meinhard type TR-30-A3
Back pressure	32 p.s.i. (1 p.s.i. = 6894.76 Pa)
Total liquid flow-rate	2.25 ml/min
Argon flow-rates	
Coolant	12 l/min
Plasma	1.4 l/min
Nebulizer	1.15 l/min
Ion lens voltages	
Bessel barrel (B)	+2.49 V (25)
Bessel plates (P)	−7.12 V (10)
Einzel lens (E_1)	−14.00 V (70)
Photon stop (S_2)	−5.03 V (25)
Resolution	0.9 amu (normal)
Torch	Sciex ''short'' torch
Interface	
Sampler	Pt cones, orifice diameter 0.040–0.045 in. (1 in. = 2.54 cm)
Skimmer	Pt cones, orifice diameter 0.030–0.035 in.
Pressures (after 1 h warm-up)	
Roughing pump system	775 Pa
Mass spectrometer	$1.78 \cdot 10^{-3}$ Pa

4.2.2. LC

IC experiments were carried out using a Dionex 4000i pump (Dionex, Sunnyvale, CA, USA) equipped with a polystyrene–divinylbenzene based ion-exchange column (see Table 3). The reversed-phase high-performance liquid chromatography

Table 2
ICP-MS analysis conditions

Instrument software	Elan 5000 Version 2.01
Sweeps/reading	10
Readings/replicate	1
Number of replicates	1500
Dwell time	10 ms
Points across peak	1
Resolution	0.9 amu (normal)
Scanning mode	Peak hop
Polarity	+
Analyte isotope	^{128}Te
Internal standard isotope	^{125}Te

(HPLC) experiments were carried out using two Gilson Model 302 pumps equipped with 802C manometric modules (Gilson, Middleton, WI, USA). The tellurium compounds were separated by means of a Nucleosil 120-5 C_{18} analysis column connected to the first HPLC pump. By means of a second pump an internal standard solution containing tellurium enriched in ^{125}Te was continuously added to the eluate of the analysis column. Sufficient back pressure was supplied to the second pump by means of 5 m polyether ether ketone (PEEK) tubing (1.58 mm O.D.×0.127 mm I.D., Deerfield, IL, USA). The HPLC set-up used is depicted in Fig. 6 and the operating and analysis conditions are presented in Table 3. The eluates from both the IC and HPLC set-up were supplied to a TR-30-A3 Meinhard nebulizer by means of 60 cm PTFE tubing (1.6 mm O.D.×0.22 mm I.D.). The HPLC–ICP-MS measurements were quantified through peak area measurements obtained by means of a Kontron MiniMOP digitizer (Kontron Bildanalyse, Munich, Germany). Also ChromafileMS software (Perkin-Elmer Sciex) has been used for this purpose. In both cases peak areas of increasing tellurium concentrations (as unretained H_6TeO_6) were used as a reference [40].

4.3. Reagents

A tellurium stock solution containing 100 mg Te/l was prepared by dissolving H_6TeO_6 (Fluka, Buchs, Switzerland) in demineralized water. This stock solution was used to prepare two sets of 10 calibration solutions. The low concentration set ranged from 20 to 200 μg Te/l in 20 μg/l increments, the high concentration set from 100 to 1000 μg Te/l in 100 μg/l increments. The internal standard solution was prepared by dissolving 2.0±0.1 mg of material enriched in ^{125}Te (ORNL, Oak Ridge, TN, USA) in 1 ml of conc. HNO_3 (Suprapur, Merck). Next, 25 ml of 1 *M* NaOH was added and the solution was diluted to 1 l. The isotopic composition of the enriched material, as determined by ORNL, and the isotopic composition of tellurium of natural origin, are given in Table 4. All other reagents used were of the highest purity available (equal to or better than analytical grade). Demineralized water was obtained from a Milli-Q system (Waters–Millipore, Bedford, MA, USA) that supplied 18 MΩ cm water quality.

Table 3
IC and HPLC operating and analysis conditions

IC

Pump	Dionex 4000i
Flow-rate	2 ml/min
Column	Dionex AG4A + AS4A
	(polystyrene divinylbenzene-based
	ion exchanger)
Injected volume	50 μl
Mobile phase	Eluent 1: 200 mg/l NaOH
	Eluent 2: 500 mg/l Na_2CO_3
	Eluent 3: 500 mg/l $NaHCO_3$
	Eluent 4: Water

Elution

Gradient time (min)	Eluent 1 (%)	Eluent 2 (%)	Eluent 3 (%)	Eluent 4 (%)
0–1.0	20	80	–	–
1.0–3.0	20	–	35	45
3.0–9.0	20	55	–	25
9.0–10.0	20	–	–	80

HPLC

Pumps	Gilson model 302 with 802C
	manometric module
Flow-rates	
Sample stream	2 ml/min
Internal standard stream	0.25 ml/min
Column	250×4 mm, Nucleosil 120-5 C_{18}
Injected volume	500 μl
Mobile phase	4% (v/v) 1-propanol in an aqueous
	solution of 10^{-2} M H_3PO_4

5. Results and discussion

5.1. Preliminary ICP-MS experiments

Freshly drained waste water was filtered, spiked with 100 μg Rh/l and then continuously nebulized
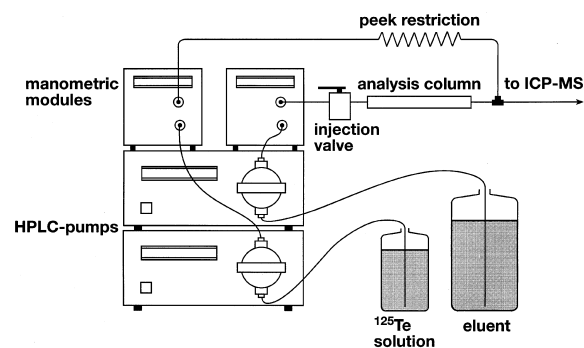

Fig. 6. Schematic overview of the HPLC set-up used.

and introduced into the ICP-MS instrument. On analyzing the same sample repeatedly a fast increasing response was observed for both isotopes selected (^{125}Te and ^{128}Te) while the ^{103}Rh response remained constant. In addition, by flushing the sample introduction system with water or dilute HNO_3, the ^{103}Rh intensity decreased rapidly (within 30 s) to the background level (<20 cps) but surprisingly, the Te isotopes did not. It took more than 90 min of continuous flushing to bring both Te intensities down to background level again. Moreover, in argon gas washed through waste water, volatilized tellurium was detected. Obviously, tellurium originating from the waste water had a quite different behaviour than (the expected) ionogenic Te^{4+} and Te^{6+}. This was confirmed by a recirculation experiment in which a 10 ml waste water aliquot was spiked with rhodium and continuously nebulized and analyzed while the liquid running down the drain was returned to the original aliquot (see Fig. 7). The behaviour of

Table 4
Isotopic composition of the material enriched in ^{125}Te and of tellurium of natural origin

Isotope	Abundance, in atomic percent	
	Material enriched in ^{125}Te	Tellurium of natural origin
^{120}Te	<0.02	0.095
^{122}Te	0.06	2.59
^{123}Te	0.09	0.905
^{124}Te	0.38	4.79
^{125}Te	93.45	7.12
^{126}Te	4.07	18.93
^{128}Te	1.16	31.70
^{130}Te	0.79	33.87
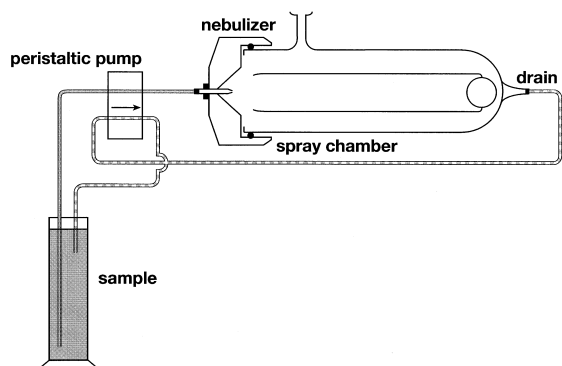
Fig. 7. Schematic representation of a recirculation experiment.

tellurium originating from a representative waste water sample is shown in Fig. 8. In this Figure both Te isotopes are presented in proportion to the ^{103}Rh
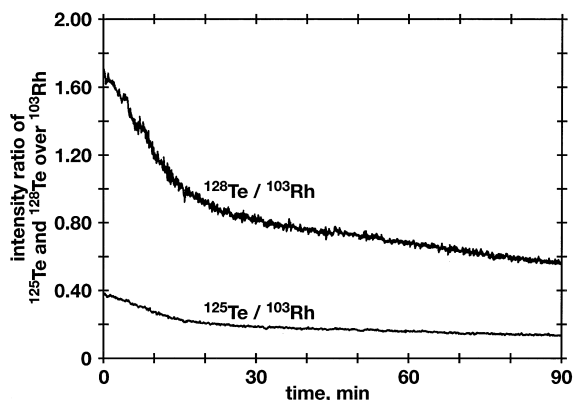

Fig. 8. Decay of ^{125}Te and ^{128}Te isotope intensities during a recirculation experiment performed with a representative waste water sample.

intensity, i.e., rhodium is used as an internal standard. Again, quite deviant tellurium behaviour was observed when compared to ionogenic Te^{4+} and Te^{6+}.

Apparently, the tellurium is "enriched" in the aerosol that is supplied to the argon plasma with a consequent decay of both Te intensities. As can be seen in Fig. 8, the intensity ratios decrease from 0.38 to 0.12 and from 1.70 to 0.55 for the ^{125}Te and ^{128}Te isotopes, respectively. The magnitude of decrease indicates that at least 70% of the tellurium present in the waste water is subject to this "enrichment" process which is commonly referred to as selective volatilization. On the other hand, at most 30% of the tellurium responds as ionogenic Te^{4+} and Te^{6+} which shows as a constant Te/Rh intensity ratio herewith indicating equal tellurium concentrations in both aerosol and drain liquid.

5.2. IC–ICP-MS

To confirm the presence or absence of ionogenic Te^{4+} and Te^{6+} a separation method by means of IC was developed whereby Te^{4+} and Te^{6+} were separated as TeO$_3^{2-}$ and HTeO$_4^{-}$, respectively. An IC–ICP-MS chromatogram of freshly drained waste water is presented in Fig. 9. The occurrence of both Te^{6+} and Te^{4+} in freshly drained waste water, eluted at retention times t_R of 5.2 and 7.0 min, respectively, was clearly demonstrated. However, both Te species proved to be superposed on a very broad slowly decaying (45 min) tellurium peak of unknown origin. All attempts to achieve adequate separation of both ionogenic Te peaks from the Te containing "basis", were unsuccessful. The tellurium compound(s) re-
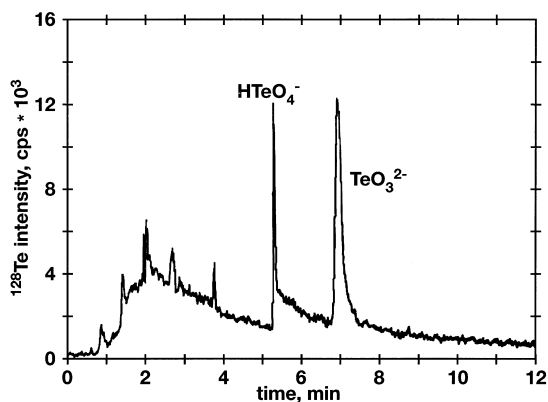
Fig. 9. IC–ICP-MS chromatogram of freshly drained waste water.

sponsible for this phenomenon were most probably adsorbed by the polystyrene support of the ion exchanger in the separation column and were then slowly and irreproducible released. A peak area comparison of the unresolved "basis" and the superposed TeO_3^{2-} and $HTeO_4^-$ peaks indicated that only a minority (14%) of tellurium was present as ionogenic Te^{4+} and Te^{6+}. Since adequate separation of the unresolved "basis" could not be accomplished it was decided to develop a reversed-phase LC separation coupled to ICP-MS.

5.3. HPLC–ICP-MS

After determining usable conditions for the separation by means of HPLC–ICP-MS, samples of freshly drained waste water were analyzed. A

HPLC–ICP-MS chromatogram of a representative waste water sample is shown in Fig. 10. Note that the y-axis is expressed as the ratio of analyte (^{128}Te) and internal standard isotope (^{125}Te) intensities. Since enriched ^{125}Te was used as an internal standard, the approach can be considered as a continuous on-line isotope dilution method, resulting in both accurate and precise quantitative results. A thorough theoretical treatment of this approach is given in Ref. [40]. Consequently, analyte suppression or enhancement in the course of a chromatogram, e.g., caused by elution of unretained inorganic constituents of the sample, was perfectly corrected for (note the change in ^{125}Te intensity between 1–2 min in Fig. 5). Additionally, instrumental drift was also compensated for, so that a calibration curve once determined remained valid during the complete analysis run. Note that the different tellurium compounds eluting from the column were superposed onto a constant background level (0.0124) originating from the residual ^{128}Te concentration in the enriched material (see Table 4). This approach is also analogous to dual-wavelength operation with flame photometric detection in HPLC and was demonstrated to be of great benefit when using detectors in gradient HPLC coupled to a nebulizer interface [41].

Under the conditions used for the HPLC–ICP-MS chromatogram of Fig. 10, the ionogenic Te^{4+} and Te^{6+} were eluted unretained at retention times t_R between 1.0 and 2.0 min. As can be seen, the majority of the tellurium detected did originate from two incompletely resolved compounds eluting between 10.8 and 13.0 min. Up to 11 tellurium
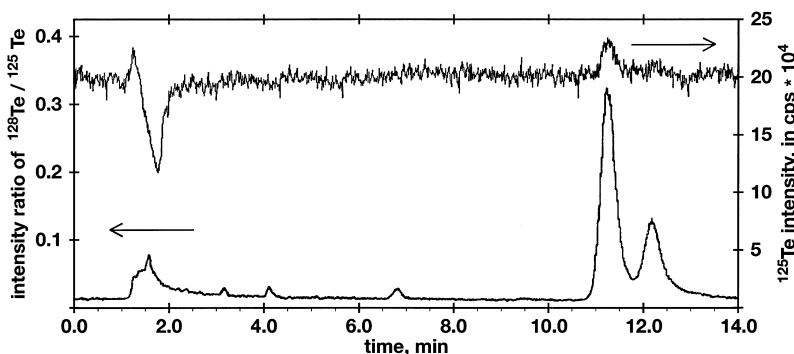

Fig. 10. HPLC–ICP-MS chromatogram of freshly drained waste water expressed as the ratio of $^{128}Te/^{125}Te$ intensities (left y-axis). The ^{125}Te intensity used as internal standard is also shown (right y-axis).

compounds have been detected in the waste water. By comparison of peak areas this was quantified as 11% ionogenic tellurium (Te^{4+} + Te^{6+}) and 89% originating from tellurium compounds. This is in good agreement with results previously obtained by means of recirculation and IC–ICP-MS experiments. It is evident that the proposed cementation process is not applicable for the removal of tellurium compounds unless they are previously converted into ionogenic Te^{4+} and Te^{6+}.

HPLC–ICP-MS chromatograms of waste water that increasingly had been ''aged'' at pH 10 revealed that the tellurium originally present as tellurium compounds, was progressively converted into Te^{4+} and Te^{6+}. Applicable conversion conditions as a result of NaOH addition were tested in terms of pH and conversion time. For that purpose, freshly drained waste water was adjusted to various pH values and subsequently analyzed by means of HPLC–ICP-MS at regular intervals. The chromatograms obtained for the pH 11.5 and 12.5 experiments are depicted in Fig. 11. In this Figure the conversion of tellurium compounds into unretained Te^{4+} and Te^{6} is clearly demonstrated. On a quantitative basis the conversion rate appeared to be a function of the initial hydroxide concentration (pH) and the conversion yield a function of the basicity and conversion time t_c. However, even at high basicity (pH = 13) and prolonged t_c (>24 h) complete conversion was not obtained. Eventually, the conversion reached an equilibrium whereby 1–4% of the tellurium remained present as compound(s) with $1.8 < t_r < 4.0$ min. Experiments at lower pH values revealed that the latter compound(s) had to be considered as intermediates in the conversion of tellurium compounds into Te^{4+} and Te^{6+}.

The different compounds detected were quantified by means of peak area determinations. As reference, a calibration graph was determined by injecting increasing Te concentrations (as H_6TeO_6 dissolved in water), eluting unretained. This type of calibration graph is curved by definition [40]. For every Te compound showing up in the chromatogram a uniform detection limit of 1 μg Te/l was obtained. The accuracy of the results was secured by the use of the enriched [125]Te-isotope as internal standard (on-line isotope dilution). The precision was determined at concentration levels of 50 and 500 μg Te/l and appeared to be 3 and 2% R.S.D., respectively.

5.4. Process conditions of Te removal

On the basis of the aforementioned experiments conversion conditions could be derived which are a compromise between the cost of NaOH supply and an industrially manageable reaction time. In view of the vast amount of waste water that had to be processed, a conversion time t_c of 2 h at a pH of 12.5 was proposed. The process conditions applied can be summarized as follows: (1) conversion time $t_c = 2$ h at pH 12.5±0.1; (2) filtering through a sand filter ($t_{res} = 0.5$ h); (3) cementation by means of iron ($t_{res} = 1$ h).

This approach was successfully tested over a period of six months. During this time elevated tellurium concentrations in the effluent were not observed. In addition, the residual Te-intermediates detectable in the waste water just before entering the iron columns, proved to be absent in the effluent. Since Te^{4+} and Te^{6+} are removed in the iron column by means of cementation, the equilibrium Te-intermediates $\rightleftarrows$ (Te^{4+} + Te^{6+}) apparently shifts in the direction of the latter hereby increasing the removal efficiency. Undoubtedly, the active pH 12.5 is a favourable condition for this.

This approach was therefore taken as the basis for a tellurium removal process engineered on plantscale, meaning that the benchscale arrangement had to be scaled up by a factor of 10^4–10^5. This uncommonly large upgrading implicitly indicated the need for close support of the plantscale start-up and introduction of the removal process in order to readjust or reestablish operating parameters whenever necessary.

6. Conclusions

Parallel to the plantscale introduction of tellurium containing catalysts the removal process plant (called telluur verwijderings installatie or TVI) was put into operation. It is evident that, in view of the scaling up factor, the performance of the TVI was thoroughly checked and fine-tuned. The pH 12.5 approach was successfully implemented in the TVI and has been used ever since.

At present, the performance of the TVI is checked on a daily basis by means of GFAAS [42] as well as less frequently by means of HPLC–ICP-MS. The
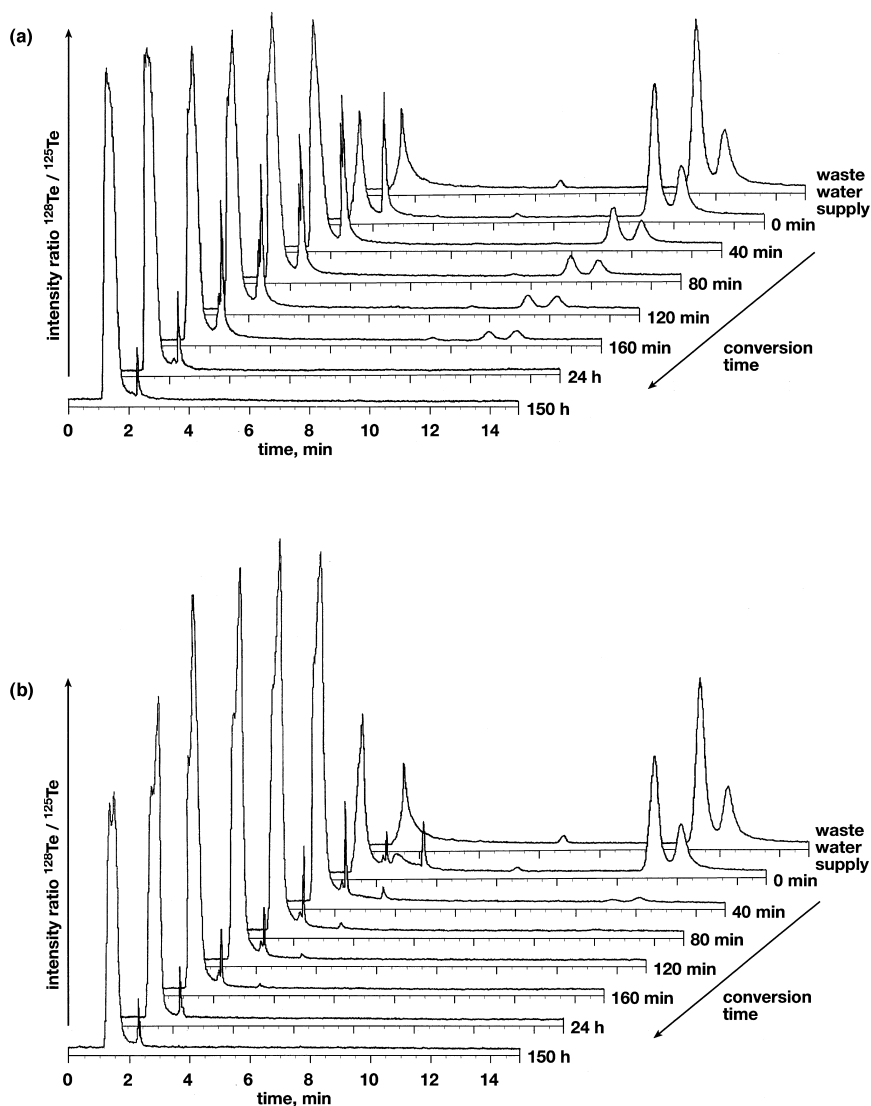
Fig. 11. (a) HPLC–ICP-MS chromatograms showing the conversion of tellurium containing compounds into Te^{4+} and Te^{6+} at pH 11.5, using increasing conversion times. (b) HPLC–ICP-MS chromatograms showing the conversion of tellurium containing compounds into Te^{4+} and Te^{6+} at pH 12.5, using increasing conversion times.

TVI has been operated successfully for several years still using the original batch of iron.

Surprisingly, the two dominating tellurium compounds showing up at the end of the chromatogram, are still not identified. The reason for this is twofold. At first, the limited stability and the low concentration of both tellurium compounds relative to the huge excess of concomitant organic compounds poses a nearly insolvable problem in an identification study. Secondly, the reliable and successful operation

of the pH 12.5 approach, although pragmatic, is not the required impulse for the quest for identify.

The relatively high NaOH concentration of the eluting waste water does not pose a problem to the central waste water purification plant. On the contrary, the operating costs of the IAZI were (slightly) decreased through a reduction in $Ca(OH)_2$ consumption, which is necessary to adjust an optimum pH for biological purification.

LC–ICP-MS has proven to be a very powerful

analytical technique in terms of sensitivity, element specificity, accuracy and precision. The technique can be used both qualitatively and quantitatively while the latter mode of operation can be upgraded to an on-line isotope dilution approach. As far as tellurium is concerned, the results achieved with this technique are by no means the optimum in terms of e.g., LC resolution attainable, nevertheless, the method described is still in use unchanged. The main reason for this is to facilitate comparison of recent results with those obtained before.

Finally, it is stimulating to notice that the in-laboratory developed tellurium removal process operates reliably within the specifications and limitations originally set during the research program and can therefore be considered as a valuable contribution to the company's policy with regard to health, safety and environment.

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