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Precise Determination of Cadmium, Indium and Tellurium Using Multiple Collector ICP-MS

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New sample preparation and ion-exchange separation methods as well as instrumental measurement protocols were established for the determination of trace-level Cd, In, and Te concentrations in geological materials by isotope-dilution mass spectrometry. High precision isotope ratio measurements were performed with a multiple collector inductively coupled plasma-mass spectrometer (MC-ICP-MS). The mass biases incurred for In and Te were corrected by adding and monitoring Pd and Sb standard solutions, respectively. Mass fractionation of Cd was corrected by using the mass fractionation factor calculated from the measurement of a standard solution. The measurement precision was better than 1% for Cd, In and Te. Detection limits were ‹ 1 ng g^{-1} for Cd, ‹ 0.02 ng g^{-1} for In and Te. Using these new analytical techniques, the concentrations of Cd, In and Te were determined in six international geological reference materials. Concentrations could be reproduced within 3% for Cd, 4% for In and 10% for Te. Sample heterogeneity and volatility problems might have been the reason for the relatively large differences between Te replicates. Our results displayed excellent reproducibility compared with those of other techniques and agree well with data from previously published recommended values.

Une nouvelle méthode de préparation des échantillons et de séparation sur résine échangeuse d'ion, ainsi que de nouveaux protocoles instrumentaux d'analyse ont été mis au point pour la détermination de très faibles quantités de Cd, In et Te dans des matériaux géologiques par dilution isotopique. La mesure très précise des rapports isotopiques a été réalisée avec un ICP-MS à multicollection. Le biais de masse pour In et Te a été corrigé en ajoutant des solutions standards de Pd et Sb. Le fractionnement de masse du Cd a été corrigé en utilisant le coefficient de fractionnement calculé à partir de la mesure d'une solution standard. La précision des mesures est inférieure à 1% pour Cd, In et Te. Les limites de détection sont ‹ 1 ng g^{-1} pour Cd, ‹ 0.02 ng g^{-1} pour In et Te. Avec ces nouvelles techniques analytiques, nous avons mesuré les concentrations en Cd, In et Te dans six matériaux géologiques de référence. La reproductibilité des valeurs est de l'ordre de 3% pour Cd, 4% pour In et 10% pour Te. Des problèmes d'hétérogénéité des échantillons et de volatilité de l'élément pourraient expliquer les différences relativement grandes entre les replicats de Te. Nos résultats présentent une excellente reproductibilité si on les compare avec ceux obtenus par d'autres techniques et sont en parfait accord avec les valeurs recommandées déjà publiées.

Keywords: cadmium, indium, tellurium, multiple collector ICP-MS, reference materials, precise determination.

Mots-clés : cadmium, indium, tellurium, ICP-MS à multicollection, matériaux de référence, déterrmination précise.

Chalcophile trace elements such as cadmium, indium and tellurium are sensitive indicators of the role of sulfides during geological processes and provide a good proxy for sulfur. The elements Cd, In and Te were measured extensively in lunar samples and some types of meteorites by instrumental neutron activation analysis (INAA) (Morrison *et al.* 1970, Anders *et al.* 1971, Krahenbuhl *et al.* 1973, Ganapathy *et al.* 1973, Wolf *et al.* 1979, Morgan *et al.* 1985). This technique, however, suffers from relatively large uncertainties (50-100%) as was demonstrated by the range of Cd and Te concentrations determined by INAA in BCR-1, a widely used geological standard reference material. Published data range from 115 to 180 ng g^{-1} for Cd (Anders *et al.* 1971, Wolf *et al.* 1979, Ganapathy *et al.* 1973, Krahenbuhl *et al.* 1973) and 4.0 to 8.2 ng g^{-1}

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for Te (Wolf *et al.* 1979, Ganapathy *et al.* 1973, Krahenbuhl *et al.* 1973). Other techniques such as AAS, ICP-AES, isotope dilution thermal ionisation mass spectrometry (ID-TIMS), flameless atomic absorption spectrometry (FAAS) and spark source mass spectrometry (SSMS) have also been used to determine these elements (Gladney *et al.* 1992) for limited applications, with variable and generally unsatisfactory precision. As a consequence of the analytical difficulties, data for trace level Cd, In and Te concentrations in geological samples are scarce, other than the aforementioned lunar samples and some meteorites. In order to obtain high quality abundance data for these elements, we have developed new ion-exchange separation procedures and established reliable instrumental measurement protocols for determinations by isotope dilution MC-ICP-MS (Halliday *et al.* 1995, Yi *et al.* 1995).

Experimental techniques

Samples

Four USGS geochemical reference materials, AGV-1 (andesite), BIR-1 (basalt), G-2 (granite) and W-2 (diabase), and two GIT-IAG reference materials, PM-S (microgabbro) and WS-E (dolerite) were analysed in this study.

Chemical separation

Hydrochloric acid (HCl) and nitric acid (HNO_3) used in this study were purified by distillation in quartz. Hydrofluoric acid (HF) was twice distilled by sub-boiling in a Teflon still. Water/H_20 was purified using a Millipore deionizing system.

We adopted the ion-exchange procedures reported by Loss *et al.* (1990) for the separation of Cd and Te (along with Sn, Pd and Ag) and have made extensive modifications to accommodate the separation of In and to improve the efficiency of the technique (Figure 1). The following is a brief summary of the sample preparation and chemical separation procedure.

About 70 mg of each sample was spiked with enriched ^{111}Cd, ^{113}In and ^{125}Te and digested with hot concentrated HF and HNO_3. About 0.05 ml of concentrated HF was used per mg of silicate. It was found that the use of HNO_3 was essential for good reproducibility in the determination of Te, although the presence of this acid may reduce the yield of the chemical separation. Therefore, the amount of HNO_3 used was reduced to 0.05 ml / 50 mg basaltic powder from 0.2 ml / 50 mg, as applied for normal silicate digestions in our laboratory. After the initial HF-HNO_3 attack, the samples were converted into chloride form and dissolved in 3 ml of 6 mol l^{-1} HCl. Total dissolution of the samples at this stage was essential to minimise the loss of Te by oxide precipitation or the escape of volatile phases.

The separation procedure included two column-chemistry stages. The first stage utilized columns filled with 0.4 ml of Bio-Rad™ AG1-X8 (100-200 mesh) anion-exchange resin. Following cleaning of the resin bed with 2 mol l^{-1} HNO_3 and equilibration with 4 ml of 6 mol l^{-1} HCl, the sample solutions were loaded onto the column. Indium was only weakly adsorbed under these conditions and could be partly eluted with 3 ml of mol l^{-1} HCl, together with alkali and alkaline earth elements, Al and a small amount of the Fe. This aliquot was saved for a second pass through the same column in order to separate In from other major elements (see below). Afterwards, a volume of about 2 ml of 2.5 mol l^{-1} HCl was passed through the column to strip off most of the Fe. The partition coefficient of Te was only slightly greater than that of Fe in 2.5 mol l^{-1} HCl. Therefore, care had to be taken to control the volume of 2.5 mol l^{-1} HCl used to elute Fe. However, since Fe contents vary by more than a factor of two, it was difficult to calibrate the small columns for separation of Fe and Te. In practice, the yellow-greenish colour of the eluting solution was used as an indicator of whether the majority of Fe had been eluted from the column. Tellurium was then collected with 3 ml of 0.5 mol l^{-1} HCl, together with the remaining Fe. This solution was processed with a second cation-exchange column to further separate Fe. A further 3 ml of 0.5 mol l^{-1} HCl was passed through the anion exchange column to elute Zn and a few other elements. Cadmium was finally collected with 3 ml of 2 mol l^{-1} HNO_3.

The In fraction of the first anion-exchange separation was evaporated to dryness, re-dissolved in 3 ml of 2.5 mol l^{-1} HCl, and loaded on the same anion column which had previously been equilibrated with 2.5 mol l^{-1} HCl. A volume of 2.5 ml of 2.5 mol l^{-1} HCl was passed through the column to elute alkaline and alkaline earth elements. Indium was then collected with 3 ml of 0.5 mol l^{-1} HCl. For samples with high Fe content, the In fraction may not be sufficiently clean to be run on a mass spectrometer. In this case, the In fraction was further processed on a cation-exchange column with a 0.4 ml resin bed of Bio-Rad™

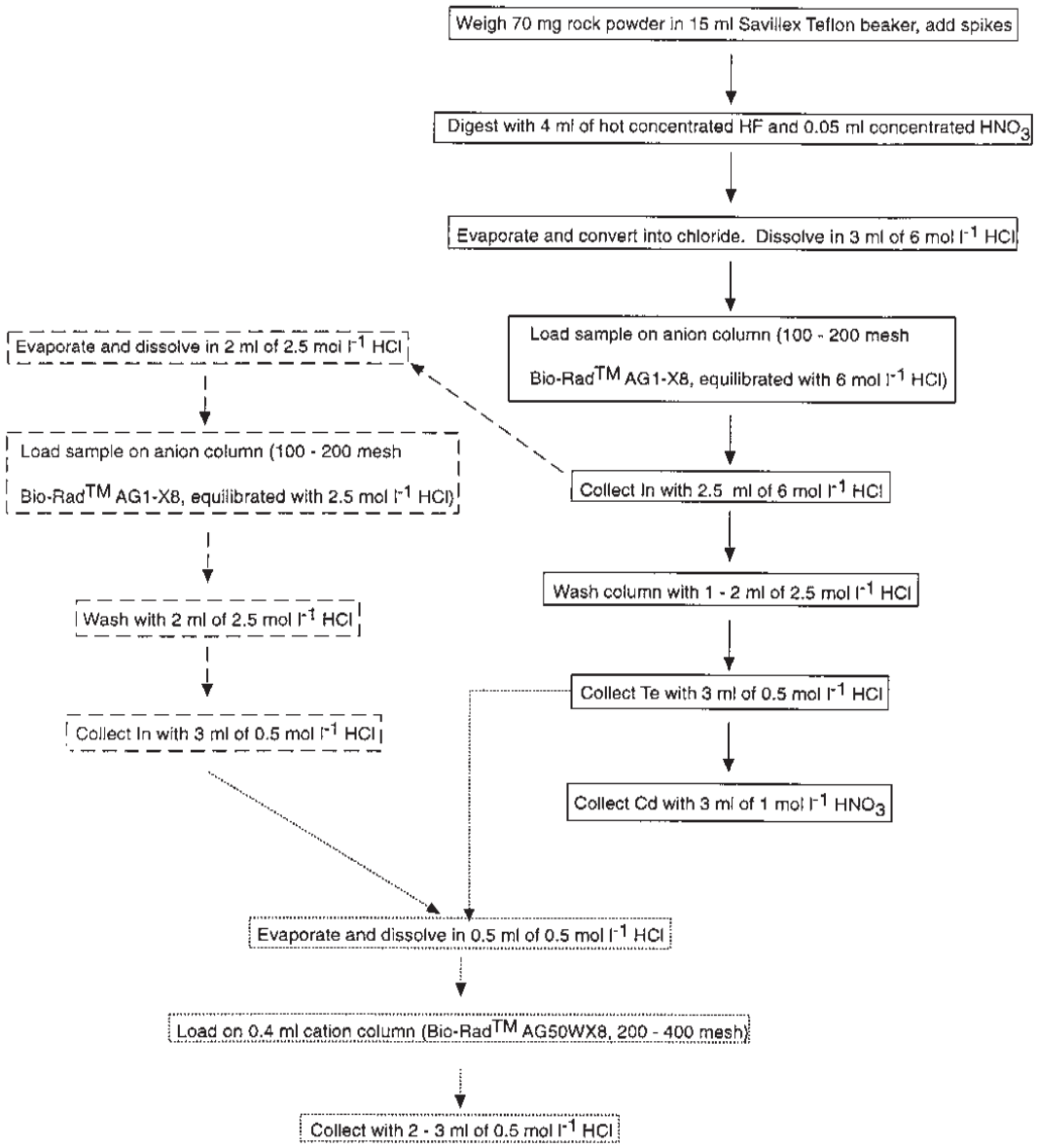

Figure 1. Schematic diagram of ion exchange separation procedures for Cd, In and Te.

AG50WX8 (200-400 mesh). After loading of the 0.5 mol l^{-1} HCl sample solution, In was collected with 3 ml of 0.5 mol l^{-1} HCl. Following this, the 0.5 mol l^{-1} HCl Te portion from the primary anion column was loaded directly onto the same cation-exchange column. While iron was strongly retained by the resin under these conditions, tellurium was not adsorbed. An additional 2 ml of 0.5 mol l^{-1} HCl were passed through the column to collect any remaining Te.

MC-ICP-MS isotope ratio measurement

Isotope ratio measurements for Cd, In, and Te were performed on a VG Plasma 54 MC-ICP-MS (Walder and Freedman 1992, Walder *et al.* 1993a,b, Halliday *et al.* 1995, Lee and Halliday 1995, Yi *et al.* 1995). This instrument utilizes an Ar plasma with a temperature of more than 7,000 K as an ion source. The high temperature achieves nearly 100% ionisation of Cd, In and Te. Minor impurities in the sample solutions can be tolerated, since they do not cause a severe reduction of ion beam intensities nor lead to the deterioration of peak shapes. A desolvating nebuliser was used for all the measurements. Early measurements were made with a VG Elemental "Mistral", whereas later measurements used a Cetac Technologies MCN6000. Working conditions for the MC-ICP-MS and Cetac Technologies MCN6000 are given in Table 1.

Table 1.
VG Elemental Plasma 54 MC-ICP-MS and Cetac MCN6000 operating conditions

Plasma 54	
R.F. power	1.2 kW
Cool Ar flow	13 l min^{-1}
Auxiliary Ar flow	0.5 - 2.0 l min^{-1}
Nebuliser Ar flow	0.60 - 0.70 l min^{-1}
MCN6000	
Spray chamber	70 °C
Desolvater	160 °C
Sweep Ar gas flow	2.8 - 3.2 l min^{-1}
Nitrogen flow	0.3 - 0.6 l min^{-1}

Cadmium, indium and tellurium are analysed using separate routines. Prior to the measurement of samples, a standard solution of the corresponding element was used to optimise the peak shape and intensity of the ion beam, to align collectors and to verify the analytical performance. Separates of Cd, In and Te were taken into solution with 2 µl of 6 mol l^{-1} HCl and diluted with 1 ml of H_2O. The solutions were introduced into the plasma via the Mistral nebuliser made from Teflon® and incorporating desolvation to prevent hydride formation. The dry analyte was carried to the plasma by a flow of Ar gas. A dose of nitrogen gas was introduced into the desolvating chamber to improve efficiency. In between measurements, the system was flushed with 5% v/v HCl until the ion beam intensity of the relevant isotopes was less than 0.1% of the corresponding analyte intensities. For the measurement of Cd, the adopted procedure also served to monitor the mass fractionation of Cd. The analysis routines for Cd and In used static run modes with Faraday cups, while that for Te used a two-step peak-jump mode, with a Daly detector always occupying the axial position. For the measurement of Te, the low collectors were arranged such that L2 and L4 were positioned at masses 123 and 121, respectively, with the axial Daly collector positioned at mass 125. L3 was positioned at mass 123 when the axial Daly collector was positioned at mass 126. The ratios of $^{125}Te/^{123}Sb$ and $^{121}Sb/^{123}Sb$ were obtained in the first step and that of $^{126}Te/^{123}Sb$ in the second. By combining the ratios of $^{125}Te/^{123}Sb$ and $^{126}Te/^{123}Sb$ to calculate the ratio of $^{125}Te/^{126}Te$, the necessity of comparing measurements on Daly and Faraday detectors (which would require the calibration of gain) was avoided.

In the plasma ion source, mass fractionation showed little variation with time. Two measurements of $^{111}Cd/^{113}Cd$ for a Johnson Matthey Cd solution performed over a period of two months produced a difference of only 0.2%. In the course of a day, mass fractionation generally varied by less than 0.1%. High concentrations of impurities could cause mass fractionation to vary, but the variations were always smaller than 0.5%. Therefore, for isotope-dilution measurements, the mass fractionation of a given element could be treated as invariant in the course of a day. The mass fractionation has been corrected in this fashion for Cd, because our Cd separation was very efficient and mass fractionation variations introduced by impurities were likely to be minimal. A mass bias measurement on a Cd standard on the same day was directly assigned to each sample.

Differences in mass fractionation between elements of similar mass were also small (Walder and Freedman 1992, Halliday *et al.* 1995, Yi *et al.* 1995, Hirata 1996). Therefore, the mass fractionation of one element can be corrected with sufficient accuracy, by applying the mass bias measured for another element of similar mass during the same run. In this fashion, the mass fractionation of In and Te were corrected by concurrently monitoring the isotopic compositions of Pd and Sb, respectively.

Discussion

The overall yield of the chemical separation procedure was better than 70% for Cd, about 30% for In, and 20% for Te, estimated by the comparison of the signal intensities between sample and standard solutions. All the elements analysed in this study can be highly volatile under laboratory conditions and this was particularly true of Te. For example, Te_2F_{10} and TeF_6 have boiling points of 53 and -38.9 °C, respectively, at atmospheric pressure, and volatile loss of Te was the main difficulty in achieving high yields. To illustrate this problem, a Johnson Matthey Te solution in concentrated HF, which was evaporated to dryness, lost 70% of its signal intensity compared with an unevaporated solution of equivalent Te concentration. Tellurium spikes, which were put through the chemical separation process, displayed a loss of signal intensity to a similar degree. It is unlikely that the low Te yield reflected the incomplete decomposition of samples, otherwise, the spike Te would display varying degrees of signal gain compared with Te contributed by the silicate samples and reproducibility and accuracy would be severely impacted. The partition coefficient for In between anion-exchange resin and 0.01-6 mol l^{-1} HCl displays only small variations, which prevented the selective elution of In. Furthermore, the chemical separation

Table 2.
Cd, In, and Te concentrations for selected rock reference materials

Sample	Cd ng g^{-1}				In ng g^{-1}				Te ng g^{-1}		
	This Study		*	Rec.	This Study	Yi *et al.* 1995		Rec.	This Study		Rec.
	Replicates	Mean†‡			Replicates	Replicates	Mean†¶		Replicates	Mean†§	
AGV-1	60.8	61.1	-	69	43	46	43.5	41	1.74	1.56	1.9
	61.4	±0.6	-	-	43	44	±1.3	-	1.38	±0.18	-
	-	-	-	-	-	43	-	-	-	-	-
	-	-	-	-	-	42	-	-	-	-	-
BIR-1	96.3	96.5	97	80	54	57	54.5	-	5.8	5.7	7
	96.7	±0.9	92	-	-	54	±1.5	-	5.6	±0.15	-
	-	-	102	-	-	53	-	-	-	-	-
G-2	15.0	14.8	-	16	26	24	25.8	30	5.2	5.2	5
	14.7	±0.2	-	-	27	26	±1.0	-	5.2	±0.15	-
	14.8	-	-	-	-	-	-	-	-	-	-
PM-S	78.4	78.3	-	110	-	47	45.5	80	3.31	3.07	-
	78.2	±0.8	-	-	-	44	±1.5	-	2.83	±0.24	-
W-2	74.3	73.2	74	104	60	63	60.5	-	1.83	1.84	2
	71.0	±1.0	79	-	-	59	±1.5	-	1.88	±0.05	-
	74.3	-	77	-	-	60	-	-	1.90	-	-
	-	-	-	-	-	-	-	-	1.76	-	-
WS-E	121	117	-	-	-	93	91.5	-	7.3	7.0	-
	115	±3	-	-	-	90	±1.0	-	6.7	±0.3	-
	115	-	-	-	-	-	-	-	-	-	-

All replicates represent separate dissolutions.
* Sands and Rosman 1997.
Rec. recommended values. From Potts *et al.* (1992) and Govindaraju (1994).
† 1s standard deviation.
‡ Minimal uncertainty ± 1%.
¶ Calculated from this study and Yi *et al.* (1995).
§ Minimal uncertainty ± 3%.

procedures were set up to maximise the yield for Te, which usually has the lowest concentration in geological samples. Therefore, our techniques achieved only a moderate chemical yield for In.

Despite the substantial loss of Te due to volatility, equilibrium between spike and sample was clearly achieved routinely, as demonstrated by the excellent reproducibility of our data for multiple dissolutions of the same sample. It appears that screw capped Savillex™ beakers incorporate a good sealing mechanism to prevent Te fluorides escaping from the beaker in the course of sample dissolution and that an HF-HNO_3 medium was suitable for achieving full spike-sample equilibration. The Te losses probably occurred during the open beaker heating which was associated with the evaporation of the presumably dissolved and homogenized sample solutions.

Both isotopes of In overlap in mass with nuclides of other elements (^{113}In with ^{113}Cd, ^{115}In with ^{115}Sn). The ^{111}Cd/^{113}Cd ratio with potential isobaric interferences from In, was selected for the calculation of Cd concentrations. Therefore, an effective separation of Cd from In is needed. Cadmium isotopes were virtually absent from separated In aliquots. The presence of a small Sn peak (‹ 1% of the In peak) during isotope ratio measurements of In was believed to be the result of inter-sample contamination (memory effect) rather than an unsatisfactory chemical separation. It was more difficult to assess directly the amount of In present in Cd separates. However, the highly reproducible Cd concentrations indicate that our Cd separates were essentially free of In. The ^{125}Te/^{126}Te ratio was used to calculate Te concentrations; ^{125}Te was free of isobaric interferences, but ^{126}Te overlaps with ^{126}Xe. While xenon may be present in the Ar plasma gas as an impurity, we observed only a negligible ^{129}Xe peak during the course of these measurements.

Total procedural blanks were less than 1 pg for Te (‹ 0.5% of sample Te), less than 100 pg for Cd (‹ 1% of

sample Cd), and less than 1 pg for In (< 0.01% of sample In). The relatively high Cd blank was mostly contributed by deionized water.

Results

The concentrations of Cd, In and Te in six international geological reference materials were analysed using the techniques established in this study. The results are listed in Table 2. Some additional data for In are from Yi *et al.* (1995).

Replicated data of Cd concentrations for three reference materials (AGV-1, BIR-1, PM-S) agree within 1%, whereas those for G-2 agree within 2%. These are typical uncertainties for Cd measurements with the techniques described in this study. Compared to the recommended values, our Cd measurements for AGV-1, G-2, PM-S and W-2 were about 11%, 8%, 29% and 30% lower, respectively. Our data for BIR-1 were about 20% higher, respectively, than recommended values. These are significant differences. However, the reproducibility, sensitivity and low blank of our techniques lead us to conclude that our results are accurate. Furthermore, our data for BIR-1 and W-2 agree well with the new TIMS data of Sands and Rosman (1997). The differences with the recommended values are most likely the result of the large uncertainties in the neutron activation analysis techniques on which the values were based. Therefore, the recommended values for these reference materials should be updated in the light of the results of this study.

Our new results for In are consistent with those reported by Yi *et al.* (1995). The range of In for AGV-1 previously reported was from 42 to 46 ng g^{-1}; new data were 45, 43, and 43 ng g^{-1}. Our previous In data for BIR-1 was from 53 to 57 ng g^{-1}; the new data are 56 and 54 ng g^{-1}. For G-2, two In data of 26 and 27 ng g^{-1} were added to the two existing data of 24 and 26 ng g^{-1}. For W-2, two In data of 60 ng g^{-1} were added to the two existing data of 63 and 59 ng g^{-1}. Our In data are generally in good agreement with recommended values except for PM-S, for which the recommended value was about a factor of two higher.

Internal deviations of the replicates for Te were all smaller than 10%. Differences between the data presented in this study and the recommended values were up to 30% (BIR-1). It is unlikely that these differences were the results of sample heterogeneity, as the replicates of this study all have much smaller variations. Although the recommended values are also measured by isotope dilution techniques, the earlier isotope ratio measurements were carried out by thermal ionisation mass spectrometry (Loss *et al.* 1983). The high ionisation potential of Te may have prevented a Te beam of adequate intensity being obtained during TIMS analysis and therefore, introduced greater uncertainties.

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