Determination of total tin in sediment reference materials by isotope dilution inductively coupled plasma mass spectrometry after alkali fusion

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The total tin concentration in a candidate sediment reference material (NIES CRM No.12 Marine Sediment) was determined by inductively coupled plasma mass spectrometry (ICP-MS) with a combination of different sample decomposition methods (acid digestion and alkali fusion) and modes of quantification [standard addition and isotope dilution (ID)] during a collaborative analysis for certification. Good agreement between the methods was obtained (10.2–11.0 mg kg^{-1}) and the data were consistent with those obtained from collaboration laboratories (9.38–11.6 mg kg^{-1}). Among the analytical methods used in this study, the most precise method, ID-ICP-MS, was examined further for its accuracy by analyzing other sediment CRMs. The analytical values obtained after acid digestion and alkali fusion differed significantly for all seven sediment CRMs analyzed; the total tin value was consistently higher and the relative standard deviation of the analysis was larger when the sample was decomposed by alkali fusion than by acid digestion. The difference varied from CRM to CRM (3–80%). This result indicated that there was a fraction of tin that was resistant to acid attack and the distribution of the fraction in the sediment was inhomogeneous. For an accurate determination of total tin in sediment, alkali fusion-ID-ICP-MS is the most suitable method.

Introduction

Tin (Sn) in geological materials has been determined in the context of ore exploitation and understanding of the geochemistry of this element. A number of methods are available for the determination of total Sn in this matrix, such as atomic absorption spectrometry (AAS),[1–6] inductively coupled plasma atomic emission spectrometry (ICP-AES)[7] and X-ray fluorescence spectrometry (XRF),[7] although the sensitivity of the last two methods is not high enough for the trace determination of Sn. Total Sn determination in geological materials has tended to be concentrated on rocks and ores and relatively little attention has been paid to Sn in sediments.

The National Institute for Environmental Studies (NIES) recently issued a marine sediment certified reference material, NIES CRM No.12 Marine Sediment, prepared for the quality assurance of organic Sn (tributyltin and triphenyltin).[8] Organic Sn compounds have been used as antifouling agents on ships' hulls and are now known to have a toxic effect on non-target marine organisms. During the certification of this CRM, collaborative analysis for total Sn content was also carried out. Four out of five laboratories that participated in the collaborative analysis for total Sn used mixed acid digestion for the decomposition of this CRM and the other used non-destructive neutron activation analysis. Since some geological materials contain acid-insoluble Sn(IV) oxide, data derived from sample decomposition by alkali fusion should also be included in the certification.

In certifying an element content in a candidate CRM, inclusion of a definitive analytical method is desirable to obtain a reliable certified value. Our laboratory has been using isotope dilution (ID) inductively coupled plasma mass spectrometry (ICP-MS) for the certification of a variety of elements in environmental and biological CRMs. Establishment of an alkali fusion-ID-ICP-MS procedure was therefore necessary for the accurate determination of total Sn in the candidate sediment CRM.

This study consisted of two parts. First, the total Sn content of NIES CRM No.12 Marine Sediment was measured by AAS, ICP-MS and ID-ICP-MS preceded by alkali fusion for the certification. Second, based on the ID-ICP-MS developed for the certification, determinations of total Sn in other sediment CRMs were carried out to examine the accuracy of the method further.

Experimental

Samples

NIES CRM No.12 Marine Sediment was analyzed for total Sn content for certification. It was prepared from a surface sediment from Tokyo Bay sampled in 1989. The detailed preparation procedure, homogeneity assessment and certification of the tributyltin content of the CRM have been described in a separate paper.[8] Sediment CRMs with certified or information values for total Sn were used for the validation of the proposed alkali fusion-ID-ICP-MS procedure. They included two CRMs from the Geological Survey of Japan (GSJ) with preferable values for total Sn:[9] Lake Sediment JLk-1 (preferable value for Sn 5.7 mg kg^{-1}) and Stream Sediment JSd-1 (2.77 mg kg^{-1}). There were also three CRMs from the National Research Council of Canada (NRC) with certified values for total Sn: MESS-1 (certified value 3.98 ± 0.44 mg kg^{-1}), BCSS-1 (1.85 ± 2.5 mg kg^{-1}) and PACS-2 (19.8 ±

2.5 mg kg^{-1}). Another CRM from NIES, CRM No.16 River Sediment for PAHs, was analyzed to determine information values for total Sn.

Reagents

ACS grade $LiBO_2$ used for fusion was purchased from Aldrich (Tokyo, Japan) and ultrapure HCl (Kanto Chemicals, Tokyo, Japan) was used for the dissolution of fusion cake. For the solvent extraction of Sn from the fused sample, trioctylphosphine oxide (TOPO) and ascorbic acid (both from Merck, Darmstadt, Germany) were used. 4-Methylpentan-2-one (IBMK) (Kanto Chemicals) and 2,6-dimethylheptan-4-one (DIBK) (Wako, Osaka, Japan) used as an extraction solvents were of AAS grade. Ultrapure HNO_3, $HClO_4$ and HF used for acid decomposition were purchased from Kanto Chemicals.

A tin stock standard solution was prepared by dissolving 0.5 g of high purity Sn metal (99.999%) (Wako) in 180 g of 30% ultrapure HCl and diluting to 500 g. Working standard solutions were prepared by diluting this stock standard solution with 1 M HCl.

A ^{118}Sn spike solution was prepared as described by Okamoto[10] and used for ID analysis. The spike concentration was accurately determined by a reverse isotope dilution technique using a standard solution prepared from the high purity metal.

Water used throughout the study was purified with a Millipore (Bedford, MA, USA) water purification system without further in-house distillation.

Instrumentation

The ICP-MS instrument used was a Hewlett-Packard (Avondale, PA, USA) HP-4500. The operating conditions were as follows: rf power 1.3 kW; reflected power, < 1 W; plasma gas flow rate, 16 L min^{-1}; auxiliary gas flow rate, 1.10 L min^{-1}; nebulizer gas flow rate, 1.15 L min^{-1}; and sample uptake rate, 0.2 mL min^{-1}. A flow injection (FI) system with a 100 μL sample loop was made from a six-way valve and Teflon tubing and was operated manually. Sample was delivered to the ICP by means of the peristaltic pump of the ICP-MS instrument.

Scannning conditions for standard addition (SA)- and ID-ICP-MS analyses were as follows: ions monitored, *m*/*z* 120 for SA and 118 and 120 for ID, integration, 1 s for SA and 3 s for ID; data acquisition, three points per mass (peak center ± 0.05 u) by peak jumping mode; and number of measurements per sample, three for SA and five for ID. The software of the HP-4500 fixes the scan number at 100; the dwell time was automatically set at 3.3 ms per point or 10 ms per mass for SA and 10 ms per point or 30 ms per mass for ID.

In the ID analysis, the within-run precision of the ^{120}Sn/^{118}Sn measurement, *i.e.*, the relative standard deviation (RSD) of the five replicates, was typically 0.3% for 20 ppb Sn standard solution (10^5 cps at *m*/*z* 118). Other major Sn isotopes, *i.e.*, 116, 117, 119, 122 and 124, were also monitored in the preliminary experiments to check if spectroscopic interferences were present. Mass discrimination was corrected by periodic measurements of a standard solution (20 ppb) prepared from pure Sn metal.

A Z-5100 Zeeman-effect background correction AAS instrument (Perkin-Elmer, Norwalk, CT, USA) fitted with an Sn hollow cathode lamp and AS-60 autosampler was also used for the determination of solvent extracted Sn.

Alkali fusion–FI-ICP-MS

The method of alkali fusion employed in this study was adopted from Elsheimer and Fries.[5] A 0.15–0.2 g amount of the sample was mixed with 0.75 g of $LiBO_2$ in a high-purity glassy carbon (Toho Carbon, Tokyo, Japan) or platinum crucible and heated in a muffle furnace at 1000 °C for 15 min. Sediment samples were precombusted at 500 °C for 4 h in a Pyrex glass beaker to remove organic carbon when a platinum crucible was used for fusion. After cooling overnight, the crucible was placed in a weighed Teflon beaker which was then filled with 1 M HCl. The fusion cake was dissolved by gentle heating and magnetic stirring. The solution was made up to 100 g with 1 M HCl and stored in a Teflon or polypropylene bottle as a stock sample solution.

An aliquot of the stock sample solution was further diluted 10-fold with 1 M HCl and an appropriate amount of Sn was added. Three point standard addition (including 0 ng addition) was employed. The sample was analyzed by FI-ICP-MS, monitoring the ion at *m*/*z* 120 in the transient signal acquisition mode. Quantification was effected by peak area integration.

Alkali fusion–solvent extraction-AAS

The procedure for alkali fusion to prepare the stock sample solution was the same as above. The subsequent solvent extraction procedure was based on that of Elsheimer and Fries.[5] An aliquot of the stock sample solution (typically 25 g) was placed in a capped 50 mL Teflon centrifuge tube and 0.45 g of ascorbic acid was added. Then 10 mL of 4% TOPO in IBMK was added and the mixture was shaken for 10 min by using a mechanical shaker. Phase separation was performed by centrifuging the tube at 3000 rpm for 10 min. The organic layer was transferred into another Teflon centrifuge tube and stored at 4 °C until measurement. The extracted Sn concentration was determined by AAS using standard solutions similarly extracted. A tungsten-impregnated graphite tube was used without any chemical modifier.[2]

Alkali fusion–solvent extraction-ID-ICP-MS

An appropriate amount of ^{118}Sn spike was added to the sample and fused as described above. After TOPO–IBMK or TOPO–DIBK extraction, 3-4 mL of the organic layer were transferred into another Teflon centrifuge tube and the Sn was back-extracted into 1 mL of 5 M HNO_3 by using a vortex mixer for 1 min. The HNO_3 layer was diluted fivefold with water and subjected to ICP-MS measurement. Total Sn concentrations in the samples were calculated from the measured ^{120}Sn/^{118}Sn ratios according to the ID equation (*e.g.*, ref. 11).

Acid digestion-ICP-MS and -ID-ICP-MS

Approximately 0.3 g of the sample (and ^{118}Sn spike solution in ID analysis) was weighed into a Teflon beaker and decomposed with HNO_3–$HClO_4$–HF. The sample solution was made up to 50 g with 0.5 M HNO_3 after heating to dryness. Standard addition-ICP-MS determination carried out using a similar procedure to the $LiBO_2$ fused sample, although FI introduction was not used. Ion counts at *m*/*z* 118 and 120 were measured directly from the ^{118}Sn spiked, decomposed and diluted solution for ID-ICP-MS quantification.

Results and discussion

Contamination

It was found, in an earlier phase of the present study, that significant contamination was present in the $LiBO_2$ fusion–TOPO–IBMK extraction procedure. The sources of the contamination were identified: glassware, reagents and the atmosphere. Leaching of Sn from glass was apparent when 1 M HCl was stored in a glass calibrated flask, although all of the glassware was vigorously washed with acid prior to use. Therefore, all of the glassware was replaced with Teflon or polyethylene vessels. The tin contents of all the reagents used were checked by ETAAS and ICP-MS. It was found that TOPO contained a significant amount of Sn as an impurity. TOPO samples from various manufacturers were surveyed for their Sn contents and the purest one, in terms of Sn impurity content, was selected and used throughout. Other reagents used did not contain detectable Sn. Some Sn contamination was found to occur on decomposing the sample in a muffle furnace. Two different muffle furnaces installed in different laboratories were tested but the results were similar. Therefore, a procedural blank was prepared for each series of sample fusions. The mean Sn contamination level in the subsequent ID-ICP-MS analysis was 11 ± 9 ng, but typically 5–7 ng when samples with 300–2000 ng Sn contents were treated. The blank level was typically 1 ng for the acid digested samples with 500–6000 ng Sn contents.

Total Sn contents of NIES CRM No.12 Marine Sediment

General. The total Sn contents of NIES CRM No. 12 Marine Sediment and NRC PACS-2, which was analyzed concurrently for quality control of the analysis, determined by a variety of methods, are given in Table 1. There were no significant differences in the mean values between ETAAS and FI-ICP-MS, both preceded by alkali fusion, and acid digestion-ICP-MS for NIES CRM No.12. A small difference was found between the values derived from acid digestion-and alkali fusion-ID-ICP-MS. All of the analytical values for NIES CRM No.12 in Table 1 were in agreement with the data from collaborating laboratories (9.38–11.6 mg kg^{-1}).[8] The variation between the data from collaborating laboratories was much larger than the small difference observed between acid digestion- and alkali fusion-ID-ICP-MS. Therefore, all of the data in Table 1 were included in the certification of total Sn in this CRM.[8] The $LiBO_2$ fusions for these samples were performed exclusively using a glassy carbon crucible.

Alkali fusion-FI-ICP-MS and alkali fusion-ETAAS. Analytical results obtained by ICP-MS and ETAAS after $LiBO_2$ fusion in a glassy carbon crucible showed a slightly poorer precision compared with those obtained after acid digestion. This is attributed to the fact that $LiBO_2$ fusion results in high, matrix (Li and B) content in the sample solution, which necessitates solvent extraction in the case of ETAAS. Involvement of solvent extraction lengthens the analytical procedure and it becomes more liable to procedural contamination. This contamination problem, together with the possible variability of the extraction efficiency, might have led to poorer precision in solvent extraction AAS analysis.

ICP-MS also suffers from the high matrix content of the sample solution prepared by alkali fusion. Although the higher sensitivity to Sn of ICP-MS did not require solvent extraction, the presence of a high matrix content necessitates the introduction of the sample by FI, which is an established sample introduction method for ICP-MS but the small sample volume (consequently small absolute amount of analyte) involved together with the high matrix concentration affects the precision of the determination.

Table 1 Results of total Sn determination of marine sediment CRMs by various methods (mg kg^{-1} dry mass)

Method	NIES CRM No.12	NRC PACS-2[a]
Fusion–extraction-ETAAS[b]	10.5 ± 0.7 (*n* = 9)	23.0
Fusion-FI-ICP-MS[b]	11.0 ± 1.0 (*n* = 5)	23.9
Fusion–extraction-ID-ICP-MS[b]	10.5 ± 0.3 (*n* = 4)	21.0; 21.6 (*n* = 2)
Acid digestion-ICP-MS	10.5 ± 0.3 (*n* = 6)	20.0 ± 1.6 (*n* = 3)
Acid digestion-ID-ICP-MS	10.2 ± 0.2 (*n* = 6)	21.5 ± 0.4 (*n* = 3)

[a] Certified value: 19.8 ± 2.5 mg kg^{-1} dry mass. [b] Alkali fusion was performed using a glassy carbon crucible.

Although the number of analyses was only one for each analytical method, the analytical results for PACS-2 by ETAAS and FI-ICP-MS were out of the uncertainty range of the certified Sn value of this CRM. This might have resulted from the poorer precision of the methods as mentioned above. Another possibility is the inhomogeneity of this CRM in terms of total Sn content, and this will be discussed later.

Alkali fusion-ID-ICP-MS. Theoretically, ID-ICP-MS provides better precision and accuracy than do other ICP-MS quantification modes. The present ID-ICP-MS result was in line with this expectation for its better precision; the RSD of the analyses of NIES CRM No.12 was 3%, which was smaller than those with ETAAS and FI-ICP-MS. However, this RSD is larger than the within-run RSD (0.3%) of the isotope ratio measurement. The poorer than expected precision might be explained by a combination of atmospheric contamination variability, as mentioned earlier, dissolved solvent in the back-extracted sample solution and sample inhomogeneity.

A preliminary experiment on the efficiency of extraction of Sn by the present procedure using a standard solution demonstrated a 99% recovery. However, the ion counts at *m*/*z* 118 and 120 for the back-extracted samples were sometimes much smaller than those for the aqueous standard solutions of a similar Sn concentration. This should have been caused by the matrix effect arising from the IBMK dissolved in the back-extracted solution. It was also possible that the presence of organic solvent in the sample might destabilize plasma. The within-run precision of isotope ratio measurement of the back-extracted sample solution sometimes exceeded 1%, which contrasted with the 0.3% RSD expected in the aqueous standard solution. This indicated that a less water soluble solvent (*e.g.*, DIBK) should be used for the extraction of Sn for more precise ID-ICP-MS determination.

The possibility of sample inhomogeneity of NIES CRM No. 12 Marine Sediment will be discussed later.

ID-ICP-MS can be an accurate analytical method only if no spectroscopic interference is present. Fig. 1 shows the ICP mass spectrum of *m*/*z* 85–130 for an unspiked NIES CRM No. 12 sample prepared by $LiBO_2$ fusion, TOPO–IBMK extraction and back-extraction. Detailed measurement of the isotope ratios of Sn in the unspiked samples revealed consistent values with IUPAC values[12] for 119/118, 120/118 and 124/118. A slight bias was found for 116/118, probably owing to molecular interference from $^{100}Mo^{16}O$ as this extraction procedure was not Sn-specific. The spectrum demonstrates extraction of Mo,

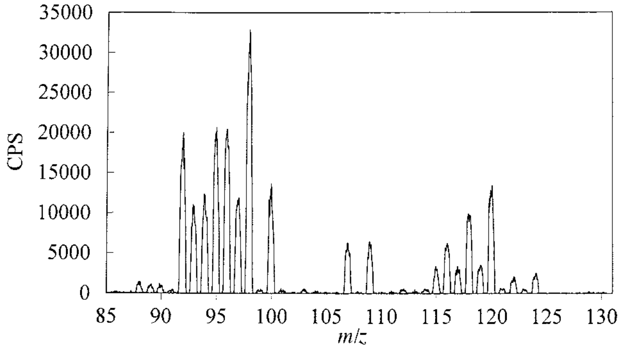

Fig. 1 An ICP mass spectrum of the *m*/*z* range 85–130 for a NIES CRM No.12 Marine Sediment sample prepared by $LiBO_2$ fusion, TOPO–IBMK extraction and HNO_3 back-extraction.

Ag and In in addition to Sn. An experiment using a standard solution showed a > 80% recovery of Mo and In by the present extraction-back extraction procedure (data not shown). Co-extraction of Mo by a TOPO extraction procedure was also reported by Terashima.[3] It should also be noted that dissolved solvent in the sample solution did not bias the mass calibration, excluding the possibility of systemtic error in the present results.

Acid digestion ICP-MS and ID-ICP-MS. The analytical values obtained by acid digestion showed a slightly better precision than those obtained by alkali fusion. This may be related to the absence of matrix arising from flux (ICP-MS) or solvent (ID-ICP-MS). The lower blank level found in the acid digestion procedure than that in the alkali fusion might also contribute to the better precision. The results for PACS-2 were in good agreement with the certified value. The co-existing elements in an acid-digested, unseparated sample did not give any spectral interference in ID-ICP-MS when a 120/118 isotope ratio was used for the quantification. Isotope ratio measurement of unspiked, acid-digested and unseparated NIES CRM No. 12 showed that some spectral interference was observed for isotope pairs other than 120/118. Interference on *m*/*z* 112, 114, 115, 116 and 119 was seen; these should be from the isobaric interference from Cd and In, but the interfering molecules responsible for the 119/118 isotope ratio deviation was not identified. Since 119/118 was consistent with the IUPAC value in the solvent extracted sample, as described earlier, a molecule containing an element unextracted by TOPO should be involved in this spectral interference on *m*/z 119.

ID-ICP-MS of Sn in other sediment CRMs

The proposed ID-ICP-MS method preceded by either acid digestion or alkali fusion was applied to the accurate determination of total Sn in other CRMs with a sediment matrix to examine the applicability of the method. For the fusion of sediments, a platinum crucible was used; precombustion of the sediment CRMs was essential to prevent insoluble platinum–tin alloy formation during the fusion process of an organic matter rich sediment.[3] The extraction solvent was switched from IBMK to the less water soluble DIBK.

Comparison of alkali fusion and acid digestion. Table 2 shows a comparison of the results obtained by alkali fusion and by acid digestion for seven CRMs. The analytical results for the CRMs were in good agreement with the certified/information values when acid digestion was employed for sample decomposition. The certified Sn contents of NRC MESS-1 and PACS-2 were exclusively based on the analytical results derived from acid digestion.[13] The recent hydride generation AAS results on NIES CRM No.16, JLk-1 and JSd-1 from GSJ were also preceded by acid digestion.[14] However, a significant difference was found between the values obtained by acid digestion and alkali fusion for all of the CRMs analyzed, the values obtained by alkali fusion being consistently higher. The absolute difference was particularly large for NIES CRM No.16 and NRC MESS-1. In addition, the RSD of the mean obtained by the alkali fusion of these CRMs was much larger (> 10%) than the expected precision of the ID-ICP-MS analysis (0.3%).

The slightly higher blank level encountered in alkali fusion than in acid digestion might only partly contribute to this variability, but it is unlikely to be the main factor. Another possibility that might be responsible for the bias and the variability was loss of Sn during fusion. Loss of Sn in the sample should apparently lead to a lower result. However, when it was combined with selective loss of an enriched isotope spike during the fusion process, it might have led to a biased result. Alkali fusion-ETAAS analysis of MESS-1, the sample with the largest difference from the acid digestion value, gave a similar result (7.5 ± 1.3 mg kg^{-1}, $n = 3$) to the alkali fusion-ID-ICP-MS value. This result shows that loss of Sn in sediment samples during fusion can be ruled out. The calculation revealed that selective loss of the enriched isotope spike would have resulted in a lower Sn value if no loss of Sn in the sample occurred. Hence loss of Sn cannot be the cause of the difference and the variability of the present alkali fusion-ID-ICP-MS results.

The results, therefore, should rather be interpreted as indicating that all of the sediment CRMs analyzed in this study contain a fraction of acid-insoluble Sn and the distribution of the fraction is inhomogeneous. The latter was unexpected in this case because the sediments analyzed in this study were all reference materials which should have been prepared to have a homogeneous element composition as a CRM.

Re-evaluation of the certified value for total Sn content of NIES CRM No.12 Marine Sediment. The small difference between the values derived from alkali fusion and acid digestion in NIES CRM No.12 Marine Sediment shown in Table 1 was reproduced. The observed small difference may indicate that this CRM also contains a small fraction of the acid-insoluble Sn. Fortunately, the difference is small enough (3%) to be covered by the uncertainty range. In addition, the RSD of the analytical result was, again, 3%, which was worse than the analytical precision of the present ID analysis (0.3%). The use of DIBK improved the within-run precision of the isotope ratio measurement of the sample solution to the level of aqueous standard solution, indicating that the deterioration of the precision due to dissolved solvent could be negligible. However, the replacement of the solvent did not improve the overall precision of analysis. It indicated that NIES CRM No.12 had sample inhomogeneity of this level (3%) in terms of Sn content at a 150–200 mg sample intake, which was also covered by the uncertainty range.

It should, therefore, be stressed that the uncertainty range of the certified total Sn content of NIES CRM No.12 Marine

Table 2 Total Sn content of sediment CRMs determined by ID-ICP-MS after acid digestion or precombustion–alkali fusion using a platinum crucible (mg kg^{-1} dry mass)

Sample	Acid digestion	Precombustion–$LiBO_2$ fusion	Certified/reference value
NIES CRM No.12 Marine Sediment	10.3 ± 0.05 ($n = 3$)	10.6 ± 0.3 ($n = 4$)	10.7 ± 1.4[a]
NIES CRM No.16 River Sediment	7.72 ± 0.18 ($n = 6$)	9.2 ± 0.9 ($n = 6$)	7.7 ± 0.1[b]
GSJ JLk-1 Lake Sediment	4.95 ± 0.04 ($n = 3$)	5.49 ± 0.07 ($n = 9$)	5.1 ± 0.2[b] 5.7[c]
GSJ JSd-1 Stream Sediment	1.82 ± 0.03 ($n = 6$)	2.14 ± 0.08 ($n = 3$)	2.1 ± 0.1[b] 2.77[c]
NRC MESS-1	3.88 ± 0.04 (n = 3)	7.0 ± 2.7 ($n = 11$)	3.98 ± 0.44[a]
NRC BCSS-1	1.95 ± 0.18 ($n = 6$)	—	1.85 ± 0.20[a]
NRC PACS-2	21.5 ± 0.4 ($n = 3$)	22.4 ± 1.7 ($n = 7$)	19.8 ± 2.5[a]

[a] Certified value. [b] Acid digestion–hydride generation AAS value from. Terashima.[14] [c] Preferable value from GSJ.[8]

Sediment includes a bias resulting from the sample decomposition method and some inhomogeneity.

The geochemical implication of the presence of acid-insoluble Sn in sediment and its inhomogeneous distribution is another issue and it will be a subject of further investigations. ID-ICP-MS will be an important tool for such investigations.

Conclusion

ID-ICP-MS was found to be a precise method for the determination of Sn in sediments. It was precise enough to detect the presence of acid-insoluble Sn in sediments at low levels (*e.g.*, 3%) when acid digestion and alkali fusion were employed for the decomposition of the same sediment sample. To obtain an accurate total Sn content of a sediment, such as in the certification of a CRM, alkali fusion-ID-ICP-MS was essential.

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