Selective Sequential Dissolution for the Determination of Inorganic Indium Compounds in the Particulate Matter of Emissions and Workplace Air

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A speciation method was developed for the determination of inorganic indium compounds in the particulate matter of emissions and from the workplace, based on selective sequential extractions. The main inorganic indium compounds that are expected to be present in the atmospheric particulate matter involving the industrial production of indium and in the manufacture of indium compounds were separated and determined. The procedure has been tested on standard reference materials. The indium recovery was in the range 93 – 105%.

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Introduction

Indium is a relatively rare non-essential metal, since no part of the world is especially rich in indium minerals. It enters into the composition of many rock-forming minerals and its overall abundance in the earth's crust has been estimated as $0.11 \mu\text{g g}^{-1}$.¹ Indium is produced mainly from residues generated during the processing of zinc ores, but it is also found in iron, lead and copper ores. It is very malleable and ductile, and can be easily formed in alloys, particularly low-melting-point alloys, which are used as fuses or temperature indicators, or in the optical industry to hold or "block" lenses during the polishing process.² Although indium can be initially more expensive than traditional solders, its physical characteristics make it a cost-effective solution to many of today's soldering and bonding challenges. Thin-film coatings, which are used in applications such as for electroluminescent lamps and for liquid crystal displays (LCDs) in flat-plan video screens, continue to be the leading end use; moreover, indium semiconductor compounds are used in infrared detectors, high-speed transistors and high-efficiency photovoltaic devices.³ Many studies have been performed on the toxicity of different compounds of indium on test animals.^{4–6} It has been recognized that toxicity depends on the physicochemical form in which it is administered. For example, exposure to InCl_3 induces DNA laddering⁷ and the alteration of cellular heme metabolism in mammalian liver.⁸ Besides, indium arsenide is both toxic and a suspected carcinogen, and though a role for arsenic can not be excluded, indium seems to be primarily responsible for these effects.⁹

A study regarding the binding of indium with human serum proteins concluded that both transferrin and albumin are responsible of indium transport in serum.¹⁰ Considering that the chemical form of the indium compounds influences bioavailability and toxicity, and that some information regarding adverse health effects to workers arising from exposure to indium compounds have been reported in literature,¹¹ a speciation procedure is gaining interest.

Indium determination can be performed with spectrophotometry, atomic absorption spectrometry (FAAS and ETAAS), optical and mass spectrometry inductively coupled plasma (ICP-OES, ICP-MS), voltammetry and neutron activation analysis. Determinations of total indium in air are well described in the literature;^{12–16} otherwise, no methods for the speciation of indium species in atmospheric monitoring are reported. Threshold levels for indium in workplaces are fixed by ACGIH (American Conference Governmental Industrial Hygienists):¹⁷ (TLV) 0.1 mg m^{-3} as total indium.

Following a scheme already used for other metal species, for example nickel,¹⁸ in this paper a sequential extractions procedure is described for the determination of the main inorganic indium compounds ($\text{In}(0)$, soluble $\text{In}(\text{III})$ salts and insoluble $\text{In}(\text{III})$ compounds) that are expected to be present in atmospheric particulate matter and in the workplace air of specific industrial production (semiconductor and optoelectronic industries) as well as in the manufacture of indium and indium compounds.

Experimental

Materials and methods

An ICP-OES Jobin Yvon JY 138 equipped with a monochromator (THR 1000) and an R. F. generator frequency (JY 2310) was used for measurements. The operating conditions and the instrumental parameters were those suggested by the manufacturer. A range of linearity between the intensity and the indium concentration ($0.4 - 10 \text{ mg l}^{-1}$) was obtained using standard solutions prepared from a 1 mg ml^{-1} stock solution, and acidified with 0.5% HNO_3 , LOD = $0.1 \text{ mg l}^{-1} \text{ In}$, LOQ = $0.4 \text{ mg l}^{-1} \text{ In}$.

Inductively coupled plasma-mass spectrometer (ICP-MS) measurements were carried out on a Perkin Elmer Mod. ELAN DRC-e instrument, following the standard procedures suggested by the manufacturer (LOD, $0.01 \mu\text{g l}^{-1} \text{ In}$; LOQ, $0.05 \mu\text{g l}^{-1} \text{ In}$).

LOD was calculated as the amount of indium which gives a signal that is 3σ of the mean blank signal and LOQ as the amount of indium that gives a signal that is 10σ above the mean blank signal.

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Airborne particulate matter was collected with an Andersen Instrumental Model 302, PM-10 high-volume sampler with $1.13 \text{ m}^3 \text{ min}^{-1}$ air flow, placed in a garden of the General Chemistry Department. Particulate matter was sampled on cellulose nitrate or acetate filters. High-volume samplings (16 h sampling, equivalent to about 1100 m^3 air) have been known to have particulate matter sufficient to test with accuracy and precision indium concentration. This matrix was used for spikes recovery.

All reagent-grade chemicals were from Aldrich Chemical Company and Alfa Aesar; Aristar-grade acids and Milli-Q water were used through the experiments.

Sample preparation

In order to have the indium concentrations nearer to those expected in the atmospheric particulate matter from the industrial production of indium and in the manufacture of indium compounds, each compound (30.0 mg of $\text{In}_2(\text{SO}_4)_3$ (13.3 mg as In), 14.3 mg of In, 20.4 mg of In_2O_3 (16.8 mg as In), 25.4 mg of In_2S_3 (17.9 mg as In) and 30.0 mg of InAs (18.1 mg as In)) was homogeneously dispersed in an agate mortar with an inert powder (200 mg SiO_2). InAs was chosen as a representative compound of semiconductor industrial production, where it can be present together with InSb and InP, because it has a similar chemical behavior. About 20 mg (exactly weighed) of each mixture was diluted with 500 mg of SiO_2 again. The homogeneity of each sample was confirmed by analyzing three sub-samples ($10 - 15 \text{ mg}$) for the total indium content (dissolution of each sample with 1 ml of HNO_3 (65%) and 3 ml HCl (37%), as below described), obtaining a recovery of between 95 and 104% with an RSD not exceeding 4%. A mixture (A) of the five species was accurately prepared by mixing in an agate mortar about 300 mg (exactly weighed) of each dispersion of $\text{In}_2(\text{SO}_4)_3$, In, In_2O_3 and about 200 mg (exactly weighed) of In_2S_3 and InAs dispersions. Three amounts (40 mg) of mixture (A) were analyzed for the total indium content and for the speciation procedure (described below) to determine their final composition. The procedure was tested both on samples prepared from pure indium compounds alone and in the presence of particulate matter collected by a high-volume Andersen sampler in the gardens of the General Chemistry Department, containing non-detectable concentrations of indium ($< 5 \text{ ng m}^{-3}$). To simplify the procedure, a similar mixture (A'), not containing In_2S_3 and InAs and, from it, two more diluted ones (B', C') were also prepared to be used for matrix spiking and recovery analyses on reference materials, where In_2S_3 and InAs were reasonably not expected. Mixture (B') was obtained by dispersing 155 mg of (A') in 845.5 mg of SiO_2 and mixture (C') from 60.1 mg of (B') in 942.8 mg of SiO_2 . Three amounts (30 mg) of mixtures (B', C') were analyzed for the total indium content and for the speciation procedure (described below) to determine their final composition. The speciation was then repeated on two reference materials: Coal Fly Ash SRM 1633 NIST (250 mg , $n = 3$), spiked with 20 mg of mixture (C') and Urban Particulate NIST SRM 1648 (250 mg , $n = 2$), before and after being spiked (20 mg C').

Blank contents on the filters, containers and reagents were accomplished to correct the final values.

Total indium determination

The synthetic samples and reference materials were treated with 1 ml of HNO_3 (65%) and 3 ml HCl (37%), sonicated for 5 min , heated with reflux for 10 min and then evaporated to a few milliliters. After cooling, the samples were filtered and made up to the mark (25 ml) with water, giving limpid solutions which were then analyzed for indium concentration. The digestion in a

Teflon bomb with HNO_3 (65%) and HCl (37%) ($1 + 3$) and a few drops of HF (48%) at 140°C for 8 h gave the same results.

Good agreement between the found and expected values in the SRMs and a good recovery in the spiked samples analyzed indicated that the total indium concentration had been correctly examined.

Speciation procedure

Weighed amounts of each sample (synthetic mixtures and reference materials) were treated with 10 ml of EDTA $6 \times 10^{-4} \text{ M}$, sonicated in a cleaner bath, 50 Hz and 305 W , for 5 min at room temperature, filtered on a $0.22 \mu\text{m}$ membrane, obtaining a solution [S_1] and a residue [R_1]. The solution that contained soluble salts of In(III) was diluted with water volumetrically (25 ml) [S_1] and analyzed for In(III) soluble.

The residue [R_1], which contained In(0), indium sulfide, indium oxide and indium arsenide, was treated with 10 ml of HCl 0.01 M and CuSO_4 0.01 M , sonicated for 5 min and filtered on a $0.22 \mu\text{m}$ membrane. In this step, In(0) was oxidized by Cu(II) to In(III). The acidity prevented indium hydrolysis and its subsequent precipitation. A solution [S_2] containing In(III) from In(0) and a residue [R_2] were obtained. The solution [S_2] was diluted to volume (25 ml) with water for the analysis of In. The residue [R_2], containing all insoluble species of indium, was refluxed for 10 min with 3 ml of HCl (37%) to solubilize In_2O_3 and In_2S_3 , and then filtered to obtain a solution and a residue. The solution was diluted to volume (25 ml) with water [S_3], and analyzed to determine In(III) from indium sulfide and indium oxide. The residue [R_3] containing InAs was refluxed for 10 min in 1 ml of HNO_3 (65%) and 3 ml HCl (37%), and then evaporated to a few milliliters. After cooling and filtration, the solution [S_4] was made up to the mark (25 ml) with water and analyzed for the indium content (indium from InAs). The residue [R_4] did not contain indium compounds. The procedure is reported in Scheme 1.

The blanks arising from each step of the dissolution procedure were evaluated and taken into account by carrying out the overall procedure step onto blank filters of the same batch used for the overall study.

Results and Discussion

The speciation procedure was tested on synthetic mixture (A) of indium compounds in the presence of particulate matter sampled from the air of gardens of General Chemistry Department, previously analyzed for the total indium content, to take into account any possible matrix influence. Particulate matter sampled on a cellulose filter was digested, as described in "Total indium determination", and analyzed by ICP-MS. We obtained a value of indium $< 5 \text{ ng m}^{-3}$, which was negligible in relation to the concentration of indium to be examined. The results of the speciation, the mean of three independent measurements, are reported in Table 1.

The procedure was then applied on spiked Coal Fly Ash SRM 1633a (consensus value for total indium, $0.16 \mu\text{g g}^{-1}$) and on Urban Particulate 1648 (consensus value for total indium, $1 \mu\text{g g}^{-1}$) from NIST, and on the same samples spiked with the indium compounds (mixture C').

Coal Fly Ash SRM 1633a ($250(\pm 0.1) \text{ mg}$) samples were digested with 1 ml of HNO_3 (65%) and 3 ml of HCl (37%) to determine the total indium concentration, which was found to be $0.19 \pm 0.02 \text{ mg g}^{-1}$, in good agreement with the consensus value. The total indium concentration was so low that speciation was not reasonably requisite; however an aliquot of the sample

Scheme 1 Selective sequential solubilization of inorganic indium compounds.

Table 1 Results of the speciation procedure on spiked particulate matter collected in gardens of the General Chemistry Department

Species	Added/ $\mu\text{g m}^{-3}$	Found/ $\mu\text{g m}^{-3}$	Recovery, %
Soluble In(III)	0.32	0.31 ± 0.02	97
In(0)	0.35	0.36 ± 0.03	103
Insoluble In(III) from In_2O_3 + In_2S_3	0.69	0.65 ± 0.05	94
InAs	0.33	0.32 ± 0.02	97
Total In (from acid digestion)	1.73	1.7 ± 0.1	98

(200 mg) was submitted to speciation, and indium could be determined only in the insoluble fraction [R_2], 0.16 mg g^{-1} (RSD ± 20), while in the other fractions it was always less than LOD (0.05 mg g^{-1}); however, in this kind of matrix, indium is reasonably expected as an oxide.

Three amounts of a certified sample (200 – 250 mg) spiked with a few mg (20 mg) of the most diluted mixture (C') containing the different indium species were submitted to the proposed speciation procedure. The results are reported in Table 2. The results of speciation, the mean values of three independent measurements, are very satisfactory.

Urban Particulate NIST SRM 1648, (85 ± 0.1) mg) was digested with 1 ml of HNO_3 (65%) and 3 ml of HCl (37%) to determine the total indium concentration, which was found to be $0.93 \pm 0.06 \mu\text{g g}^{-1}$, in good agreement with the consensus value ($1 \mu\text{g g}^{-1}$).

Two fractions of the certified sample (240 – 250 mg) spiked with a few mg (20 mg) of the most diluted mixture (C')

Table 2 Results of the speciation procedure of indium on spiked Coal Fly Ash SRM 1633a

Species	Indium added as $\text{In}/\mu\text{g g}^{-1}$	Indium found as $\text{In}/\mu\text{g g}^{-1}$	Recovery, %
Soluble In(III)	0.54	0.53 ± 0.05	98
In(0)	0.63	0.66 ± 0.05	105
Insoluble In(III) from In_2O_3	0.74	0.69 ± 0.07	93
Total In (from acid digestion)	1.91	1.9 ± 0.1	99

Consensus value for total In, $0.16 \mu\text{g g}^{-1}$; found, $0.19 \pm 0.02 \mu\text{g g}^{-1}$.

Table 3 Speciation procedure of indium on Urban Particulate NIST SRM 1648 and spikes recoveries

Species	Indium found as $\text{In}/\mu\text{g g}^{-1}$	Indium added as $\text{In}/\mu\text{g g}^{-1}$	Indium found as $\text{In}/\mu\text{g g}^{-1}$	Rec., %
Soluble In(III)	< 0.05	0.54	0.51 ± 0.05	94
In(0)	< 0.05	0.63	0.61 ± 0.06	97
Insoluble In(III)	0.92 ± 0.09	0.74	1.7 ± 0.2	102
Total In (from acid digestion)	0.93 ± 0.06	1.91	2.8 ± 0.2	98

Consensus value for total In, $1 \mu\text{g g}^{-1}$; found, $0.93 \pm 0.06 \mu\text{g g}^{-1}$.

containing the different indium salts were submitted to the proposed speciation procedure. The total concentration of indium from the speciation procedure ($0.92 \pm 0.09 \mu\text{g g}^{-1}$) was in very good agreement with that from acid digestion ($0.93 \pm 0.06 \mu\text{g g}^{-1}$) (see Table 3). All of the indium in the Urban Particulate NIST SRM 1648 was found in the insoluble fraction [R_2]; indeed, also in this kind of matrix, indium is reasonably expected to exist as an oxide.

Since indium is produced mainly from residues generated during zinc ore processing, Zn, Pb, As and Cd compounds, mainly as oxides, are expected to be present in the atmospheric particulate collected from industrial production areas at higher concentrations than indium. The two reference materials analyzed with the proposed procedure contain these compounds in greater amounts than indium (as an example, NIST SRM 1648: Zn (0.48%), Pb (0.65%), As (0.01%), Cd (0.008%)). The good results obtained make us able to rule out their possible interfering effects.

Conclusions

The procedure described in this paper allows the determination of different chemical species of inorganic indium, which can be air dispersed in emissions and working areas at concentration values lower than that fixed by law for the total indium.¹⁷ The method, essentially based on sequential dissolutions of the sampled matrix, provides a preliminary indication for the need of improved analytical techniques for measuring not only the total concentration, but also the different species of indium dispersed in contaminated air, to which a different toxicity is related. The procedure has been successfully applied to spiked air particulate matter sampled in the gardens of the General Chemistry Department, containing not a detectable indium concentration, and to environmental standard reference materials. The indium recoveries of the different species were in the range 93 – 105%.

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