Leaching of Gallium from Coal Fly Ash, Alumina and Sediment Samples with an Acid Mixture for its Determination by ICP-OES

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ABSTRACT: Leaching of gallium (Ga) from coal fly ash, alumina and sediment is reported for its determination by inductively coupled plasma optical emission spectrometry (ICP-OES). A mixture of acids (H_2SO_4 , HNO_3 and HF) was used for the leaching process which was carried out overnight at room temperature or heated for 1 h on a hot plate. HF is essential for the quantitative recovery of Ga from coal fly ash. Leaching with either HCl or HNO_3 in combination with HF also yielded quantitative recoveries of Ga from coal fly ash, but not from other matrices. After leaching, HF and HNO_3 were evaporated and HCl was added to the acid leach before dilution for analysis. When mixed acid leaching was employed, leaching of Ga was 92–102%. For accuracy, the method was applied to a sediment sample, a candidate material prepared as the in-house CRM, and the values obtained were well within the uncertainty reported. The present procedure was validated using the solvent extraction method. The values by the two methods were in close agreement according to the Student's t-test with a confidence level of 95%. The limit of detection was 0.45 mg Kg^{-1} . The analytical methodology was applied for the determination of Ga in three coal fly ash samples, two from thermal power plants and a NIST CRM 1633b (not certified for Ga) as well as an alumina sample from an aluminum industry facility. A red mud sample, by-product of Bayer's process of aluminum extraction, was also analyzed using HCl/HF and HNO_3/HF leach.

INTRODUCTION

Gallium (Ga) is a chemical element that is relatively rare and has been used largely in the electronics industry. Ga does not have its own ore and in nature occurs in trace amounts as Ga(III) compounds, principally in bauxite (aluminum matrix) and zinc ores.^{1,2} Due to the limited natural resources and the growing demand, there may be global competition for the production of Ga and hence, alternate resources need to be evaluated for economic reasons.³ Ga can also be found in coal, with approximately 10 million tons of Ga contained in the coal resources on earth.⁴ The content of Ga in coal varies regionally. Coal fly ash is a solid residue obtained after combustion of the coal in thermal power plants. This by-product is toxic due to the presence of organic and

inorganic constituents of varying compositions depending on the grade of coal. Production of coal fly ash is very high, considering that 40% of the electrical power is generated through combustion of coal globally.⁵ India is among the top three countries in the world that utilizes coal-fired power plants.⁶ The majority of coal fly ash is unutilized and stored in ash ponds and surface impounds, increasing the threat of contamination to both underground water and also air. Constituents of coal fly ash can be extracted based on their utility and also commercial value. Ga is one such constituent and due to its efficient optical transitions and also electron mobility, it is recognized as a very important component in the preparation of compound semiconductors used in photovoltaic cells.⁷ Prior to engaging in large-scale recovery, the coal fly ash samples need to be screened for their Ga content to establish the commercial value

for extraction. A simple analytical methodology is needed to carry out such screening. Another important source of Ga is bauxite, an aluminum ore. Gallium is extracted from the by-product of aluminum extraction process and is present at the mg kg⁻¹ level both in coal fly ash and in alumina. Hence, a preliminary screening procedure applicable to both types of samples would help in selecting a suitable lot for extraction that yields economic benefits.

Most of the recent papers on coal fly ash are dedicated to protect the environment from toxic constituents or the bulk recovery of the precious metal from coal fly ash.^{8,9} Zhao *et al.*⁷ reported sulfuric acid leaching of Ga from coal fly ash for the subsequent sequential recovery of Ga using P507 and Cyanex 272. Gutiérrez *et al.*¹⁰ reported leaching of Ga with HCl for sequential extraction using Amberlite LA-2 and LIX 54N. Different acid extractions are carried out with the ultimate aim of bulk extraction using foam, Cyanex, phosphate-based extractions, *etc.*

Gallium is determined by instrumental techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Direct determination of Ga by these techniques is hampered by the matrix elements that affect recovery and precision, and also the restriction on total dissolved salts in the sample solution for analysis by ICP. Slurry sampling electrothermal-AAS is the simplest method for the determination of Ga in coal fly ash and does not require any sample treatment. However, the relative standard deviations (RSD) reported are higher despite the fact that quantifications are carried out against aqueous standard calibration since there is no matrix effect.¹¹ Solvent extractions are extensively used for the extraction of Ga from 6M to 9M HCl solution since Ga forms anionic GaCl₄⁻ at higher acidities.¹²⁻¹⁴ It requires total dissolution of the sample and also uses toxic organic solvents, such as isopropyl ether, diethyl ether, acetylacetone, 5, 4-methylpentan-2-ol, tributyl phosphate, *etc.*

Recently, the ultrasonic assisted dispersive liquid-liquid microextraction method was developed for the solvent extraction of Ga for its determination in vanadium titanium magnetite.¹⁵ Similarly, the determination of Ga in alumina is also important to recover the precious metal. Gallium in Al is determined along with other elements after separation of aluminum from alumina solution by precipitation for its determination by ICP-OES.¹⁶ Multi-stage leaching steps are reported using HNO₃/HF/HClO₄ and Zheng Fang reported an HCl leach method with fewer recoveries.^{7,17} A simpler procedure with easily adaptable steps and applicable to both CFA and alumina is useful for preliminary screening of the different sample lots for the recovery of Ga.

The aim of the present work was to develop a simple leaching method for the preliminary screening of coal fly ash, alumina and other samples for Ga prior to large-scale recovery. Conditions for the quantitative recovery and analysis of different coal fly ash samples, alumina and a sediment sample are reported, along with

a red mud sample.

EXPERIMENTAL

Instruments

An inductively coupled plasma optical emission spectrometer (ICP-OES), Model ULTIMA 2, Horiba Jobin Yvon, France, equipped with a concentric pneumatic nebulizer and cyclonic spray chamber, was used for all measurements. The spectrometer is equipped with a Czerny-Turner monochromator using a 2400 grooves/mm holographic grating. The wavelength (294.364 nm) selected for Ga was based on sensitivity and lack of spectral interference.

Reagents and samples

Analytical reagent grade chemicals were used throughout. HCl, HNO₃, H₂SO₄ and HF were procured from Merck, India. Milli-Q water (Millipore Corporation, USA) with 18M Ω cm resistivity was used for the preparation of all solutions. The stock standard solution (1000 mg L⁻¹) of Ga was procured from Merck, Germany.

The coal fly ash samples were obtained from thermal power plants. The alumina and red mud samples were obtained from a local aluminum producer. A sediment was used as a candidate for reference material, and the value reported is recommended by the producer by adopting a different procedure. All samples were processed as received.

Analytical procedure

An accurately weighed sample (0.25 g) was taken into a PFA container with screw cap. Added were 1 mL each of H₂SO₄, HNO₃ and 0.5 mL HF, then left standing overnight or heated on a hot plate at about 100 °C for 1 h in closed conditions. After opening the screw cap, the acids (HF and HNO₃) were evaporated on a hot plate. The same can also be carried out on a platinum crucible. In such case, it can be heated until the appearance of thick H₂SO₄ fumes. After cooling, 1 mL HCl was added to the residue, heated for about 5 min and diluted with Milli-Q water to 25 mL along with the undissolved solids. The same procedure was applied for all samples. Blank solutions were also prepared as above, excluding the sample. For only the coal fly ash and red mud samples, a combination of either HCl/HF or HNO₃/HF was used for the same quantity of sample, then following the same analytical procedure as above.

Complete dissolution of coal fly ash and sediment

To 0.25 g of sample taken into a platinum crucible, 1 mL H₂SO₄ and 2 mL HF were added and left standing overnight. HF was evaporated on a hot plate until H₂SO₄ fumes appeared. To the residue, 25 mL HCl was added and diluted to 50 mL with Milli-Q water which resulted in a clear sample solution. If required, additional HCl was added and diluted to a higher volume. In case of the NIST coal fly ash sample and to ensure the complete

dissolution of the very minute amount of residue left, it was fused with lithium metaborate and dissolved in a minimum amount of HCl, then was added to the sample solution.

Solvent extraction of gallium

Ga in sample solutions taken in 6M HCl was extracted into diethyl ether with equal volumes of aqueous and organic layers. Ga extracted into diethyl ether was stripped back into 0.01M HCl, evaporated on a water bath to volatilize residual diethyl ether, and analyzed by ICP-OES. The blank solution was also prepared as above.

RESULTS AND DISCUSSION

Gallium does not have its own ore and is present at trace levels in bauxite, an aluminum ore. Hence, Ga is extracted from the by-product (obtained at an aluminum industry facility) or from other sources such as coal fly ash where it is present at the tens of mg kg⁻¹ level. Lots containing higher concentrations of Ga are preferred for better yield. Hence, secondary sources of Ga need to be analyzed for Ga prior to bulk extraction. Direct determination of Ga from these samples after total dissolution is difficult by instrumental techniques for want of sensitivity and also due to matrix interferences. For the determination of Ga, solvent extraction is normally adopted to pre-concentrate the analyte, while simultaneously reducing matrix interferences. However, the procedure is tedious as it involves total dissolution of the sample, followed by solvent extraction using toxic organic solvents. Moreover, residual organic solvents will extinguish the plasma if analysis is carried out by ICP-based techniques. Evaporation of the residual solvent is an additional step. Acid leaching is a better alternative to solvent extraction. Though leaching methods with different combinations of acids are reported, they either result in fewer recoveries or are used for bulk extraction.

Acid Leaching of Gallium

Initially, leaching of Ga from coal fly ash was reported by using 7M H₂SO₄. However, the recovery of Ga was found to be very poor, <5%. Hence, a combination of acids for leaching was attempted with coal fly ash, obtained from the National Thermal Power Corporation (NTPC), by oxidizing mineral acids, H₂SO₄ and HNO₃ for initial attack of the samples, and resulting in very poor recovery of Ga (30%). Based on previous experience and to increase recovery, a small amount of HF was added.^{18,19} It was found that addition of 100 µL HF improved the recovery of Ga to 60% (for 0.25 g of CFA). Hence, HF was optimized ranging from 100 to 600 µL for 0.25 g of coal fly ash sample. The recoveries are calculated based on true value of Ga obtained by ICP-OES (14.9 mg kg⁻¹). As shown in Table 1, the recovery of Ga increased with the HF concentration and maximum recovery was obtained between 400 to 500 µL. For further studies, the concentration of 500 µL HF was used.

Table 1. Amount of HF Required to Leach Ga from 250 mg of Coal Fly Ash (CFA) in Presence of 1 mL each H₂SO₄ and HNO₃

Sample No.	Volume of 48% (w/v) HF (µL)	Concentration of Ga in NTPC CFA (mg kg ⁻¹)	Recovery (%) ^a
1	100	9.0	60.4
2	200	12.6	84.5
3	300	13.5	90.6
4	400	15.1	101.0
5	500	15.2	102.0
6	600	13.5	90.6

^aRecovery with respect to value obtained by ICP-OES, 14.9 mg kg⁻¹.

Table 2. Comparison of Concentrations Obtained by Present and Solvent Extraction Methods

Sample	Leaching method	Solvent extraction
NTPC-CFA	15.3 ± 0.3	14.1 ± 1.1
IMMT-CFA	44.4 ± 2.1	45.0 ± 1.2 ^a
NIST-CFA 1633b	57.5 ± 1.8	55.2 ± 4.0 ^a
GSI Sediment (SSS1)	22.4 ± 2.3	24.4 ± 3.9 ^b
Alumina	38.0 ± 1.0	39.0 ± 1.0

Uncertainties are expressed as standard deviation of three measurements.

^aanalyzed directly; ^bindependent method.

Along with 1 mL each of H₂SO₄ and HNO₃, 500 µL HF was added to 0.25 g sample for quantitative leaching of Ga. Nitrate vapors appeared after the addition of HF. All of the acids, except H₂SO₄, were evaporated and 1 mL HCl was added since Ga has an affinity to HCl. The leach and the solid were transferred into a polypropylene (PP) vial and diluted to 25 mL with Milli-Q water for analysis by ICP-OES. External calibration was used for quantification. As there is no coal fly ash CRM available and certified for Ga, a CRM candidate sediment material was analyzed, whose Ga concentration is indicated by the CRM producer, for accuracy. The concentration obtained by the present method and the same reported by the CRM producer was within the uncertainty mentioned (Table 2).

Since the method was validated for sediment, a similar silicate matrix, the method was applied to three coal fly ash samples and one alumina sample. The alumina sample was selected in order to explore the possibility of applying the method to alumina also. The concentrations obtained are shown in Table 2. The values obtained on real world samples are validated by using the solvent extraction method after total dissolution. For total dissolution of coal fly ash, normally NaOH fusion or microwave digestion methods are adopted to ensure complete dissolution. In this study, a simple method was adopted using a mixture of acids and a hot plate for heating as mentioned in the experimental section.

For solvent extraction, sample solutions of coal fly ash and alumina taken in 6M HCl were used. A suitable aliquot was taken and Ga extracted with an equal volume of diethyl ether. Gallium from the ether layer is back-extracted into 0.01M HCl solution. The solution was analyzed for Ga after evaporating the ether, since the presence of an organic solvent will extinguish the plasma during ICP-OES analysis. The results obtained by solvent extraction

Table 3. Comparison of Concentrations of Ga Obtained by Leaching with Different Acids

Sample	Leaching method		Total dissolution
	HCl + HF	HNO ₃ + HF	
NTPC-CFA	15.6 ± 0.4	15.3 ± 0.3	14.9 ± 0.1
NIST-CFA 1633b	45.7 ± 2.0	49.5 ± 0.7	55.2 ± 4.0
GSI Sediment (SSS1)	15.4 ± 0.8	16.8 ± 0.3	24.4 ± 3.9 ^a
Alumina	40.0 ± 2.0	31.5 ± 0.5	39.0 ± 1.0
Redmud	95.0 ± 2.3	89.6 ± 3.0	98.0 ± 3.0

Uncertainties are expressed as standard deviation of three measurements.

are close to the developed method with a 95% confidence level according to the Student's t-test. The results are shown in Table 2. The limit of detection, calculated as the signal equal to three times the standard deviation (six measurements) + blank, was 0.45 mg Kg⁻¹. The concentration of Ga in the samples analyzed was in the range of 15-98 mg kg⁻¹.

In order to reduce the number of acids for leaching Ga, a combination of HCl/HF and HNO₃/HF was tested. It was found that the recoveries are quantitative in case of coal fly ash and red mud. Red mud was considered since the above procedure could not be applied due to the complete dissolution in mixed acids. The procedure was further simplified by using either of the acid combinations; however, it is suitable only for coal fly ash and red mud (Table 3).

CONCLUSIONS

A simple method is reported using mixed acid leaching of Ga from coal fly ash, sediment and alumina. The leach solution was analyzed for Ga by ICP-OES. The wide scope of the method, applicable to silicate matrices and also alumina, makes it a promising application for preliminary screening of Ga. The accuracy of the method was verified by analyzing sediment samples by an independent laboratory using an independent method. Validation of the method was carried out by solvent extraction. The method is further simplified by reducing one acid, however it is suitable only for coal fly ash and red mud. The proposed method is simple and can be adopted for screening samples for Ga content.

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Notes

The authors declare no competing financial interest.

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