

## Determination of lanthanides (La, Ce, Nd, Sm) and other elements in metallic gallium by instrumental neutron activation analysis

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### Abstract

This paper reports the analytical results of lanthanides and other elements in pure elemental gallium. The analyses were performed by instrumental neutron activation analysis (INAA) at the nuclear reactor IEA-R1, IPEN, São Paulo. INAA has the advantage of being a multi-elemental and non-destructive analytical method. After irradiation, the samples were set aside for some days before running high resolution gamma spectrometry with a hyper-pure Ge detector. Gallium was recovered from the Bayer process alkaline leach solution, named by local aluminum industry as ‘weak soda’, (spent liquor) with a concentration of about  $150 \text{ mg l}^{-1}$ . As a first step, gallium was recovered from the ‘weak soda’ and enriched using a complexing ion-exchanger of the polyamidoxime type specially synthesized in the country for this purpose. After washing the column with water and then with pure sodium hydroxide to remove the interstitial ‘spent liquor’, gallium was eluted from the resin. The eluted gallium solution was made to  $4 \text{ mol l}^{-1}$  in NaOH and subject to electrolysis. The metal was then collected from the electrodes and given a final purification step by dilute inorganic acid stripping. The most representative lanthanide elements found and analyzed in the metallic gallium were La, Ce, Nd and Sm. One of the most recent samples exhibited the following results: ( $\mu\text{g g}^{-1}$ ) La (16.1), Ce (15.5), Nd (11.8) and Sm (3.6). Besides the lanthanides, the following elements were also analyzed: U, Cr, Fe, Co, Zn, Mo, Se, Sb and Ba. The results showed that the metal obtained is highly pure. The purity can be enhanced by stripping the metallic gallium with a dilute mineral acid.

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### 1. Introduction

Primary sources of gallium are scarce; all of its production comes from secondary sources, such as the aluminum industry. Gallium follows the aluminum in its bauxite ores whose content is from 20 to 80 ppm. In the Bayer process about 70% of the gallium is leached from the bauxite and follows the aluminum into the caustic soda solution, the remaining 30% being disposed with the red mud. Gallium accumulates in the Bayer liquor due to several recyclings, reaching a concentration of  $100\text{--}200 \text{ mg l}^{-1}$ .

Gallium is a vital material in the semiconductor industry. It is mainly used in the form of arsenide and phosphide, GaAs and GaP, respectively. Analog integrated circuits have been the largest end-use application for gallium in wireless communication systems. Gallium is also used in the manufacture of light-emitting diodes, in

solid-state lasers, especially in telecommunication systems with optical fibers. Gallium arsenide is also a promising material for solar cells and for computer memories.

Ab initio experiments [1] in the Mining Department of Escola Politécnica, São Paulo State University, laboratory started with Kelex-100, but for practical reasons the solvent extraction was postponed in favour of a solid ion-exchange process.

In this paper, the possibility of using instrumental neutron activation analysis for the determination of some impurities in highly pure metal gallium was examined. The well known accuracy and sensitivity of NAA has made it a reference technique. This analytical technique offers advantages over other analytical methods in that it is multi-elemental and non-destructive, eliminating the ‘blank’ of the analysis.

Neutron activation analysis has been applied to determine several elements, including the rare earths, viz. Ce, La, Nd, Sm, and Ba, Co, Cr, Fe, Mo, Se, Sb, U and Zn as well in high-purity elemental gallium. The alkaline solution containing gallium as gallate in sodium hydroxide

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before the electrolysis was also analyzed by instrumental neutron activation analysis. In this paper the non-destructive activation analysis was used. All the elements depicted in Tables 4–7 were analyzed via instrumental neutron activation analysis.

## 2. From bauxites to metallic gallium

### 2.1. Brazilian bauxites and their Bayer liquors

Brazil has an important alumina and aluminum industry due to its large bauxite deposits. A review of Brazilian bauxite deposits made by Carvalho et al. [2] presented the principal characteristics of these deposits.

Most of our work was done with liquors which originated from Companhia Brasileira de Alumínio–CBA, located at Cidade Alumínio, São Paulo. The alumina mills process bauxites from Poços de Caldas and Cataguazes, Minas Gerais, mines. In these processes most of the vanadium and rare earths go to the red mud and the Bayer liquor is poor in vanadium and rare earths but rich in gallium.

Atomic absorption spectroscopy, fluorescence X-ray, emission spectroscopy and conventional wet chemical analyses were applied to analyze major and minor constituents of the bauxite ore and liquor used for Brazilian industrial production of aluminum. The major constituents in bauxite are aluminum, iron, silicon, titanium and organic matter (humic acids). Minor assayed elements of interest, especially concerning the Bayer liquor, are gallium, vanadium, molybdenum, copper, zinc and rare earth elements. Ion exchange chromatography with chelating resins and solvent extraction were used as the main processes for the separation chemistry.

Table 1 presents the average chemical composition of the Bayer liquors produced industrially by three Brazilian mills.

After the production of the alumina, the CBA's spent Bayer liquors have the average chemical composition depicted in Table 2. This material is being worked on at the Mining Department of Escola Politécnica, São Paulo State University, for the preparation of metallic gallium.

Table 1  
Average chemical composition of Bayer liquors from three Brazilian alumina mills

Metal	Concentration (mg l <sup>-1</sup> )		
	Mill 1	Mill 2	Mill 3
Fe	9.09	10.6	8.04
Cu	0.53	0.96	0.48
Cd	1.35	1.65	1.50
Ni	9.60	12.5	10.5
V	128	142	115
Mo	18	84	<200
Ga	55.8	149	107

Table 2  
Typical composition of a spent Brazilian Bayer liquor

Compound	Concentration (g l <sup>-1</sup> )
NaOH	160.0
Ga	0.15
Al <sub>2</sub> O <sub>3</sub>	80.0
Organic matter (as humic acids)	8.0
Density (g cm <sup>-3</sup> )	1.220
V	0.14
Mo	0.265
Zn	<0.001
Fe	0.01

### 2.2. Recovery of gallium from the spent liquor

The process comprises the use of a chelating home-made ion-exchange resin [1,5]. This resin contains amidoxime groups [3], which form chelate bonds to gallium [4]. After extracting gallium from the alkaline liquor with the mentioned resin, the column is rinsed with pure sodium hydroxide to remove the interstitial solution. The resin exhibited great selectivity in relation to gallium. Vanadium and molybdenum, also present in the liquor, were not absorbed by the chelating resin. The selectivity for gallium over aluminum is excellent, only traces of aluminum and no vanadium plus molybdenum were coabsorbed.

Gallium is finally eluted with a dilute alkaline solution. The eluted solution is then treated to separate the ultimate traces of organic matter (humic and fulvic acids). The eluted solution is acidified to a final pH 1.8–2.0, at room temperature, and after aging for a period of no less than 2 h, the humic acids were separated by filtration. This solution is refined by percolation through a macroporous copolymer (XAD-16™). From this solution gallium is concentrated via ion-exchange and precipitation and a final alkali treatment before it is sent to the electrodeposition. This is done, after adding some EDTA.

### 2.3. Reduction to metallic gallium

Metallic gallium is currently produced by electrolytic process. For many years the electrolytic process depended on the fact that mercury forms an amalgam with gallium from which the gallium may be extracted with a caustic soda solution. The gallium amalgam can be produced either directly or indirectly. The gallium is deposited directly onto the mercury cathode; using the appropriate conditions of temperature, agitation and current density, an amalgam is formed. In another process, sodium amalgam is used to reduce the gallium present in the Bayer liquor, directly. This gives an amalgam from which the gallium is removed by treatment with caustic alkali and the mercury is then used again to produce sodium amalgam, i.e. the mercury circulates in a closed system.

The environmental problems associated with mercury

further discourage the use of electrolytic gallium amalgam processes. The Brazilian process uses no mercury. It is a clean technique and does not damage the environment.

#### 2.4. Electrowinning of gallium

Gallium is produced by electro-deposition from an alkaline solution. The electrolysis is conducted in the presence of very small amounts of aluminum as the main impurity and minor amounts of other elements like iron, molybdenum, chromium, zinc, cobalt, and rare earth elements. The final concentration of sodium hydroxide was as high as 4 M.

Gallium is recovered by electrolysis using an anode made from a metal which ideally does not introduce undesirable impurities in the alkaline gallate solution under the conditions of gallium electrolytic deposition. The cathode is also made of a metal. Several metals have been tested in our laboratory. Final choice has, until now, not been made.

### 3. Determination of impurities in metallic gallium by neutron activation analyses

Fifty to 100 mg of the samples (except batch #28 after acid scrubbing, which weighed about 500 mg) were accurately weighed in polyethylene bags. The elemental synthetic standards of the analyzed elements were prepared by pipetting convenient aliquots of standard solutions (SPEX) onto 1-cm<sup>2</sup> pieces of Whatman No. 40 filter paper. The standards were sealed in polyethylene bags.

The synthetic standards were validated by irradiation with the geological reference materials BE-N (IWG-GIT) and NIST SRM 2704 Buffalo River Sediment, which have certified and recommended values for the elements analysed, giving results within 95% confidence limits.

Samples and standards were irradiated for 8 h at a thermal neutron flux of  $10^{12}$  n cm<sup>-2</sup> s<sup>-1</sup> at the IEA-R1m nuclear reactor of IPEN. The measurements of the induced gamma-ray activity were carried out in a GX20190 hyperpure Ge detector (Canberra). The multi-channel analyzer was a 8192 plug-in-card in a PC computer. The resolution (FWHM) of the system was 1.90 keV for the 1332 keV gamma-ray of <sup>60</sup>Co. Countings were performed about 10 days after irradiation and the distance between samples and detector was 10 cm. Counting times varied from 1 to 10 h. The gamma-ray spectra were processed by using the VISPECT software, which locates peak positions and calculates the energies and net areas. There was no correction for gamma-ray self attenuation by the gallium, since this contribution was considered small in relation to the errors due to counting statistics, and in only one case the weight of the sample was 500 mg. The radioisotopes used to determine the analyzed elements and their main nuclear characteristics are shown in Table 3.

Table 3  
Radioisotopes used and their main nuclear characteristics

Element	Radioisotope	Half-life (days)	Energy (keV)
Ba	<sup>131</sup> Ba	11.5	496.3
Ce	<sup>141</sup> Ce	32.5	145.4
Co	<sup>60</sup> Co	5.24	1332.2
Cr	<sup>51</sup> Cr	27.8	320.0
Fe	<sup>59</sup> Fe	45.1	1098.6
La	<sup>140</sup> La	47.27 h	328.6
			1595.4
Mo	<sup>99</sup> Mo	66 h	140.6
Nd	<sup>147</sup> Nd	11.1	91.4
			531.0
Se	<sup>75</sup> Se	119.8	136.0
			264.7
Sb	<sup>122</sup> Sb	2.70	564.2
	<sup>124</sup> Sb	60.2	1691.0
Sm	<sup>153</sup> Sm	47.1 h	103.2
U	<sup>239</sup> Np	2.35	277.5
Zn	<sup>65</sup> Zn	245	1115.4

Table 4

Trace elements in the sodium gallate before electrodeposition of Ga (errors associated with the results are one standard deviation considering counting statistics)

Element	Concentration (mg l <sup>-1</sup> )
La	18.1±0.2
Ce	65.2±0.8
Nd	64±2
Sm	13.8±0.2
Ba	1948±96
Cr	4.6±0.8
Fe	41.8±0.4
Mo	27±8
U	215±2
Zn	615±2

In Table 4 are the results of some elements determined directly in a representative gallate solution just before the electrowinning of gallium. All elements were determined by non-destructive instrumental analysis (INAA).

Table 5 depicts the analyses of two experiments where

Table 5

Two analyzed gallium samples obtained by electrolysis where the electrodes suffered corrosion (errors associated to the results are one standard deviation considering counting statistics)

Element	Concentration (µg g <sup>-1</sup> )	
	Batch #8	Batch #10
Ce	0.12±0.03	1.75±0.05
Co	0.32±0.01	1.96±0.03
Cr	23.1±0.2	39.1±0.3
Fe	123±5	370±9
La	0.82±0.04	2.51±0.07
Mo	1.2±0.2	10.9±0.5
Nd	<0.2	0.52±0.07
Sm	<0.01	0.38±0.01
Zn	37.5±0.7	73±1

Table 6

Determination of trace impurities in some representative elemental gallium samples (errors associated with the results are one standard deviation considering counting statistics)

Element	Concentration ( $\mu\text{g g}^{-1}$ )		
	Batch #25	Batch #26	Batch #27
La	<0.05	11.4±0.8	<0.05
Ce	<0.07	<0.07	<0.07
Nd	<0.2	5.3±0.5	2.4±0.2
Sm	<0.01	<0.01	<0.01
Cr	11.8±0.3	2.9±0.1	1.3±0.1
Fe	100±10	27±3	<10
Co	0.81±0.03	0.12±0.01	<0.01
Zn	17.7±0.7	18.5±0.5	7.2±0.4
Se	<0.07	0.15±0.04	<0.07

the metallic electrodes suffered some electrocorrosion. Especially iron and chromium were codeposited with gallium and contaminated the metal.

Table 6 shows the results of the analyses of some recent representative elemental gallium samples obtained after the exchange of the electrodes. In Table 7 are shown the results obtained for gallium sample #28, which was further cleaned with an acid treatment. This procedure is beneficial and contributed to partial or total decontamination of the impurities analyzed.

#### 4. Conclusions

Gallium is produced by electro-deposition from an alkaline solution. The electrolysis is conducted in the presence of a small amount of aluminum as the main impurity and minor amounts of other elements such as iron, molybdenum, chromium, zinc, cobalt, and rare earth elements. The concentration of sodium hydroxide was as high as 4 M.

A highly efficient process for producing metallic gallium

Table 7

Determination of trace impurities in a gallium sample submitted to acid treatment (errors associated with the results are one standard deviation considering counting statistics)

Element	Concentration ( $\mu\text{g g}^{-1}$ )	
	Batch # 28	Batch #28 after acid scrubbing
La	16.1±0.9	10.2±0.8
Ce	15.5±1.0	<0.07
Nd	11.8±1.1	<0.2
Sm	3.6±0.3	<0.01
Cr	49.4±0.8	<0.15
Fe	265±7	0.55±0.23
Co	1.19±0.02	<0.01
Zn	<1	51.1±0.7
Sb	8.5±0.2	2.2±0.9

from a gallium-containing sodium aluminate solution circulating in the Bayer process is briefly described here. The process comprises subjecting an alkali aluminate solution containing dissolved gallium from bauxite to a percolation operation into a complexing ion-exchanger. Gallium is preferably adsorbed from the aluminate solution and, after scrubbing the resin with appropriate solution, it is eluted. Finally, gallium is separated from small amounts of aluminum and traces of other elements by electro-deposition.

A process for extracting and purifying the gallium contained in an industrial solution of sodium aluminate by fixing the gallium on a stationary phase constituted by porous home-made complexing ion-exchanger adsorbent resin is in operation at bench-scale. After elution of the gallium, the resultant gallium salt solution is purified and concentrated so as to be reduced directly to the state of high purity metallic gallium by electrolysis. Subjecting the concentrated and purified gallium solution to electrolysis led to metallic gallium.

Before the electrolysis, organic impurities, especially humic and fulvic acids, are removed from the alkali gallate solution by acid precipitation and refined by means of a special cross-linked absorber.

The determination of trace impurities in gallium samples have been made by ICP-MS, GDMS (glow discharge mass spectrography) and INAA (instrumental neutron activation analysis). This last procedure operating at the IPEN Radiochemistry Division allowed the determination of several elements, including four rare earths: lanthanum, cerium, neodymium and samarium.

The analytical results for some samples of gallium which has been obtained by electrolysis from sodium hydroxide medium show that the metal is highly pure. The decontamination of the impurities from metallic gallium is also enhanced by stripping with a dilute mineral acid.

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