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Ion Chromatographic Determination of Gallium by Mixed Ion Exchanger

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Abstract

A progressing procedure is offered for determining of Gallium at low levels in two geological samples using High Performance Ion Chromatography technique (HPIC). At the optimum operating conditions determined experimentally, isocratic elution of gallium was 8mM pyridine-(2,6)-dicarboxylic acid eluent concentration (PDCA) at pH of 4 and flow rate of 0.7mL/min. Two granite geological samples from Gabal Gatter and Gabal El Sela-Qash Amer area have been applied for direct determination of gallium by applying the modified method. The method permits the evaluation of gallium without an external preconcentration or complexing agents.

Keywords: determination; gallium; mixed ion exchanger; IC; granite geological samples
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1 Introduction

Gallium is considered a technology-critical element and so emerged as an important strategic metal [1]. The major uses of gallium are in the renewable energy, telecommunications, and electronics sectors [2-5]. Also, it is significantly used in the fabrication of semiconductor gadgets for photovoltaic cells and computer systems on account that it offers environment friendly optical transitions in addition to excessive electron mobility [6-9].

Gallium is commonly related with Al, Zn, and Ge. Acid sulfate solutions from hydrometallurgical manufacturing of Zn are considered an essential supply of gallium, as well as alkaline Bayer solutions for Al [10]. The uncommon running prerequisites of nuclear energy reactors demand the use of uncommon coolants. Thus, one needs a coolant, gallium, which acquires a low cross section for neutrons absorbing, appropriate heat-transfer efficiency, a low melting point and a high boiling point [11].

Through the earlier two to three decades, gallium compounds have a positive effect on the field of medicinal drug and clinical applications. For instance, in clinical medicine especially in most cancers and problems of calcium and bone metabolism, radioactive gallium and steady gallium nitrate have been applied as diagnostic and therapeutic operators [12].

In the majority of the silicate rocks and minerals, gallium has been regarded as one of the trace elements, so its level of concentration reached to a little part per million (ppm). The growing use of gallium compounds in the digital enterprise and their anti-tumor pastime [13] are motives for increasing its touchy analytical methods. In latest years, a number of methods have been said for the evaluation of gallium, spectrophotometric [14-16], chromatography [17], electrothermal-AAS [18], ICP-AES [19], ICP-MS [20,21], X-ray fluorescence spectrometry [22], graphite furnace-AAS [23,24], calorimetry [25], AAS [26], fluorimetry [27] and paleography [28].

The intention of this paper is developing a method for gallium separation and determination directly in different geological samples using mixed ion exchanger by DX-500 Ion Chromatograph. For this purpose, the technique was optimized in opposition to the eluent pH, concentration and flow rate using certified soil sample (NCS DC 73325). Furthermore, the developed method has been applied for gallium evaluation within a pair of geological materials.

2 Experimental

2.1 Apparatus

Gallium was assessed quantitatively using High Performance Ion Chromatograph (HPIC), Dionex DX500 (Sunnyvale, CA, USA) equipped with UV-VIS detector (AD20), eluent delivery pump (GP40) connected to a postcolumn reagent system, and pneumatic controller. Ion-exchange separating column composed of a guard column IonPac CG5A linked to the analytical separator column IonPac CS5A which possesses unique bilayer latex structure consisting of both anion- and cation-exchange retention mechanisms.

The pH measurements were made on a digital Jenway pH meter (UK).

2.2 Reagents

All solutions have been organized by nanopure water (18.2 MΩ-cm) (Thermo Fisher Scientific Inc., USA). Standard solutions of Ga(III) have been prepared by diluting stock solutions of 1000 ppm. Mobile phase of Pyridine- 2, 6-dicarboxylic acid (PDCA) (Merck, Germany) has been used in the current study. 0.112g/L of 4-(2-pyridylazo) resorcinol (PAR) solution (BDH, UK) was employed as post-column reagent and prepared via acetic acid and ammonia solution (Panreac Quimica, SP).

2.3 Chromatographic Conditions

Isocratic elution using PDCA eluent has been achieved for gallium(III) analysis. The worked eluent was prepared in chosen ammonia buffer solution. The flow rate of both mobile phase and post-column reagent solution is adjusted at 0.9 and 0.5 mL/min respectively after preliminary optimization.

2.4 Geological Materials Characterization

The optimized advanced procedure was applied for the analysis of pair of geological samples of different contents and locality. These involved granite samples from Gabal Gattar and Gabal El Sela-Qash Amer areas which their locality is described in Table 1.

Table (1): Description of Gabal Gattar and Gabal El Sela-Qash Amer locations

Region Name	Location	Ref	Latitudes	Longitudes
Gabal Gattar	A part of the Arabian-Nubian shield and is located in the north Eastern Desert of Egypt	[29]	26° 52´ & 27° 08´ N	33° 13´ & 33° 25´ E
Gabal El Sela-Qash Amer	South Eastern Desert of Egypt at a distance of about 50 km South Western of Abu Ramad city near to the Sudanese border	[30]	22°17′44″ - 22°18′10″ N	36°13′28″ - 36°14′27″ E

2.5 Preparation of the Certified and Geological Samples

Four mixtures of concentrated acids (hydrofluoric , nitric , sulfuric and perchloric acids) have been added to 5g of the certified soil sample and 2g of each of the two geological samples for their digestion and evaporation till dryness. The obtained residues were dissolved in a nitric acid solution of ratio of 1:1. The mixtures were gently heated, cooled to room temperature. After complete dissolution, drops of hydrogen peroxide (an oxidizing agent) were added to each solution. The filtrate of the certified soil sample and the two worked samples were diluted to 25mL using deionized water (18.2 mΩ-cm). Finally, the resulting solutions from the latter are ready for analysis.

2.6 Preliminary and Method Calibration Curves Preparation

Preliminary calibration curve for Ga(III) was organized by diluting 1000 ppm of Ga (III) stock solution with different volumes according to the required concentrations. Ga(III) calibration curve for the worked developed method was prepared using the certified soil sample . So, standards solutions with different volumes have been prepared according to the required concentrations (1-6 ppm) in 10 mL volumetric flask.

3 Results and Discussions

In a prior paper, a method was developed to investigate the retention behavior of heavy metals and rare earth elements using pyridine-(2,6)-dicarboxylic acid and oxalic/diglycolic acid mixture respectively by CS5A mixed ion exchange column[31]. According to the previous study, optimal conditions have been considered as a preliminary investigation for gallium(III) determination via IC technique using; a) 7mM PDCA b) Ion Pac CS5A separation column c) PDCA eluent flow rate of 0.9 mL/min e) eluent pH of 4.1 d) PAR coloring reagent of flow rate of 0.5 mL/min for Ga(III) ion detection at wavelength of 530 nm

Quantitative measurement of gallium certified soil sample (NCS DC 73325) has been confirmed by its validation using the former protocol. It was established that, gallium(III) determination (25 ppm) is not conformable with the mean value (39.5 ppm) delivered through the China National Analysis Center for Iron and Steel using ICP-MS method.

Accordingly, gallium determination using (IC) procedure necessitates developing the technique mentioned above for optimizing the separation and determination of gallium certified soil sample (NCS DC 73325). This included series of runs such the effect of pH mobile phase, concentrations of PDCA, eluent flow rate, and ultimately effect of interfering ions in the certified soil sample.

3.1 Effect of pH of PDCA Mobile Phase

Optimization of pH of PDCA mobile phase for the determination of the separated gallium using IC technique was performed at variable pH ranging from 3.7-4.1 using buffer solutions while, mobile phase molarity of 7mM PDCA and 0.9 mL/min eluent flow rate stay steady. The output information offered in Figure 1 illustrates the pathway of pH change with the separated gallium concentration which represented in the chromatogram. Looking at the pH curve, increasing pH from 3.7-4.1 offset by increasing in the determined gallium up to pH 4 followed by decreasing the measured value therefore, the selected optimum pH was 4 which achieved 33ppm of gallium concentration in the certified soil sample.

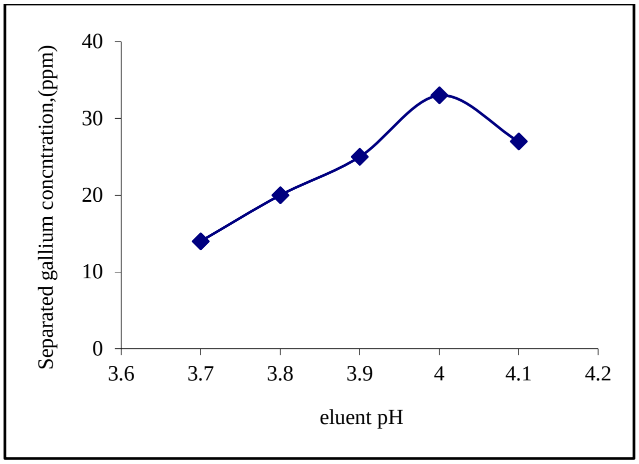

Fig (1): Influence of eluent pH on gallium separation

3.2 Effect of Eluent Concentration

To assess the capability of PDCA to elute and quantify Ga(III), the concentration of the mobile phase was varied from 5.5 to 8 mM whereas other components namely; mobile phase pH was adjusted at 4 and 0.9 mL/min eluent flow rate stay fixed.

Referring to Figure 2 it was found that variation of PDCA concentration affects the elution process of Gallium ion separation of the certified soil sample. Raising the PDCA concentration from 5.5 to 8 mM companied by raising in the separated gallium concentration and registered the greatest separation and quantification of 38ppm at 8mM concentration range of PDCA after which no value for gallium was recorded due to its overlap with the neighbor (iron) which is directly separated after gallium. So, 8mM PDCA concentration was taken to be the optimum eluent concentration for separation and determination of Ga(III).

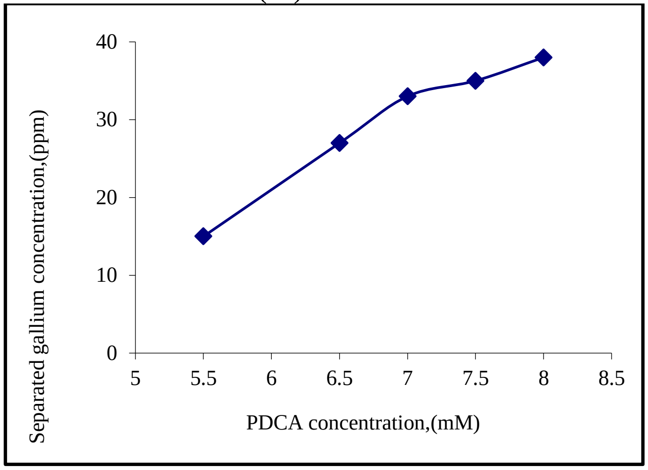

Fig (2): Influence of variation of PDCA concentration on gallium separation

3.3 Effect of Eluent Flow Rate

Using the above optimization conditions, the influence of the eluent flow rate on gallium separation and evaluation was investigated at different flow rates starting from 0.6 to1 mL/min. Figure 3 indicates that, there is a positive relationship between the PDCA flow rate and the measured gallium concentration till reached 0.7 ml/min flow rate (equivalent to 39 ppm of gallium) after which the separated gallium concentration decreased. Accordingly, the preferred optimum eluent flow rate was 0.7 mL/min.

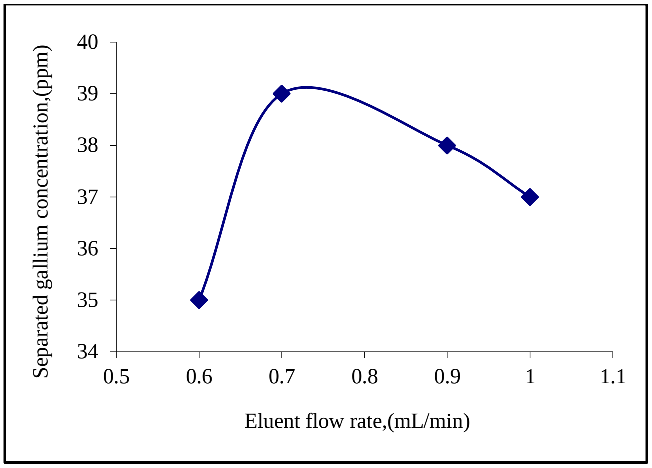

Fig (3): Influence of eluent flow rate on gallium separation

3.4 Effect of the Interfering Cations

In order to evaluate the probable analytical application of the advanced method, the influence of some foreign ions was examined. Since Ga(III) represented by the certified soil sample was separated and evaluated by complexation with PDCA , it was important to study the interferences from the other cations. It is well known from the preliminary previous study [31] that the PDCA mobile phase has the ability to elute certain of cations so, according to the worked developed method, elution of gallium using the above optimized conditions of 8mM PDCA mobile phase, pH of 4 and 0.7mL/min flow rate represented a unique separation without any interference with the nearest eluted ion (Fe) as indicated in Figure 4.

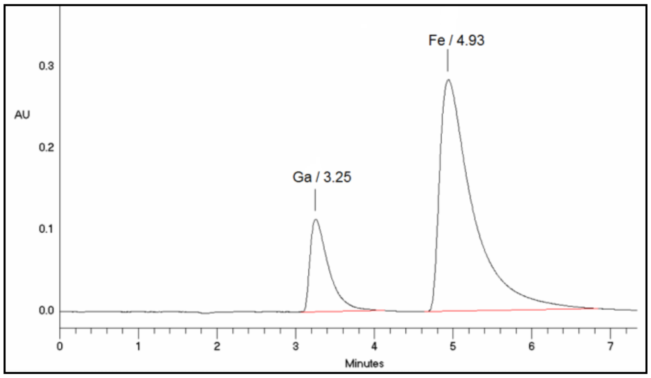

Fig (4): The chromatogram represented the separation of gallium and the nearest interfering iron

Depending on the presented chromatographic outcomes, the operated mixed ion exchanger (CS5A) offered a reliable and perfect analysis of the validator certified soil sample.

Thus, the last optimized operating conditions for Ga (III) evaluation through HNO_3 medium are described below.

Guard column - IonPac CG5A (4 x 50 mm)
Analytical column - Ion Pac CS5A (4 x 250 mm)
Eluent - 8 mM PDCA
Eluent pH 4
Flow rate - 0.7 mL/ min
Injection volume - 50μL
Postcolumn reagent - PAR
Detection Wavelength - 530 nm

Table 2 expressed the isocratic run application of gallium optimized method whereas Figure 5 clarified the separated gallium peak produced after injection of the certified soil sample

Table (2): The optimized isocratic program of the developed procedure applied for gallium separation in the certified soil sample

Time (min)	8mM mobile phase (PDCA), (%)
Initial	100
0.0	100
7	100

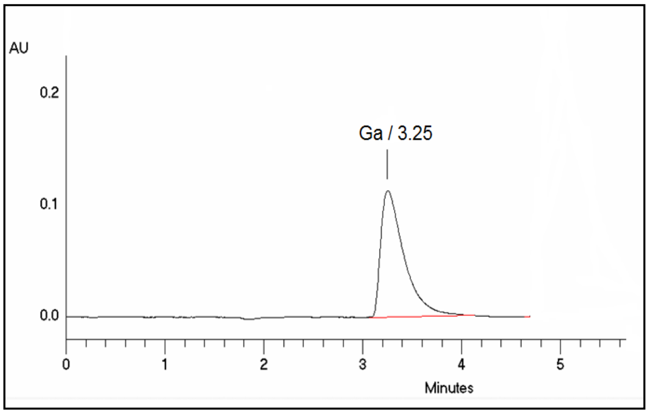

Fig (5): Separated gallium peak produced after injection of the certified soil sample (NCS DC 73325).

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3.5 Calibration Curve of the Optimized Developed Method

As soon as the working procedure for separation and determination of gallium using certified soil sample (NCS DC 73325) approved by China National Analysis Center of Iron and Steel, (Beijing, China) is optimized, the calibration curve of the studied gallium ion "Ga(III)" was performed through different concentrations of gallium certified solutions assaying from 1 to 6 ppm. A linear relationship with 0.998 regression coefficient has been produced in Figure 6.

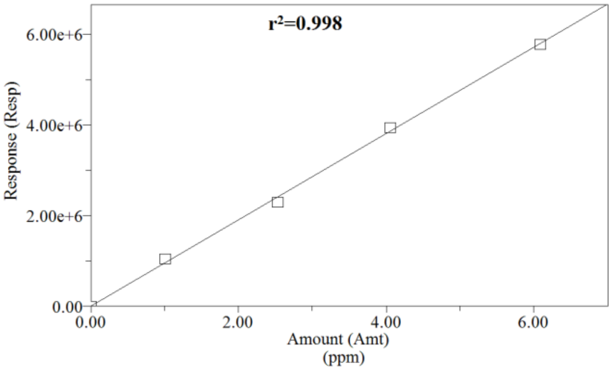

Fig (6): Gallium Standard calibration curve of the certified soil sample of the optimized developed method

3.6 Performance of the Developed Method

By calculating the Relative Standard Deviation of gallium, the overall performance of the developed technique has been installed through several injections. The relative deviation of gallium in the worked certified soil sample recorded ± 0.12 % throughout a number of injections of ten. For 50μL injection volume the detection limit stated for gallium was about 0.03 ppm.

3.7 Analysis of the Geological Samples

The studied sophisticated optimized procedure was applied for the analysis of gallium in two granite geological samples from Gabal Gatter and Gabal El Sela-Qash Amer area. The values obtained for gallium ion were determined and registered in Table 3

Table (3): Analytical results of Gallium in Gabal Gattar and Gabal El Sela-Qash Amer granite samples

Element	Gabal Gattar Granite Sample, (ppm)	Gabal El Sela-Qash Amer Granite Sample, (ppm)
Ga (III)	20 .8	32.5

4. Conclusions

In the current study, the ion chromatographic separation and determination parameters of gallium were carried out through the certified soil sample (NCS DC 73325). Application of the studied developed protocol was performed using two granite geological samples. The outcomes obtained confirmed a gorgeous separation of gallium. The approach is accurate, featured, quickly and allows evaluation of gallium within about 4minutes.

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