Determination of zinc in high purity gallium by differential pulse anodic stripping voltammetry

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A simple voltammetric method has been described for the determination of trace amount of zinc in high purity gallium metal. Differential pulse anodic stripping voltammetry (DPASV), permits a direct determination of zinc without preliminary enrichment or separation process. Zinc can be determined to levels of 1-2 μg g⁻¹, with relative standard deviation of about 14% in ≤ 150 mg sample of gallium. The detection limit was restricted by the amount of zinc present in the reagent blank solution. The possible interferences due to Pb, Cd, Cu, Ni, Mn, Fe, Ti, Co, Ti, V, Al etc. have also been evaluated.

Ultrapure gallium is of importance in electronics as well as in semiconductor devices. It is often widely recognised that the variable and often poor quality of semi-insulating substance is one of the major limitations of the present development. Characterization and certification of high purity gallium is necessary as zinc is usually present as an impurity even after several purification steps to produce high purity gallium. Work dealing with the determination of zinc by differential pulse anodic stripping voltammetry (DPASV) in varied matrices has increased in recent years. Differential pulse anodic stripping voltammetric technique has been applied successfully for the determination of zinc in air particulate matter, water samples and biological materials. A good sensitivity and selectivity is required for the analysis of zinc at trace levels in gallium matrix because the reduction potentials of zinc and gallium are very close and also there is a possibility of intermetallic compound formation between the two. Determination of various metallic impurities like chromium, indium and cadmium in gallium and gallium arsenide using voltammetric techniques has been reported. However, there is no report on direct determinations of zinc in high purity gallium matrix. Kaplin et al. have reported the determination of Te, Sn and Zn in micro amounts in high purity gallium by inversion voltammetry, but they have determined zinc only after extraction separation of gallium. A few reports can be found in literature where Ga(III) is deliberately added in high concentrations to determine Zn(II) in the presence of Cu(II) to prevent Zn-Cu intermetallic compound formation. Although the concentration of Ga(III) added is about hundred times more than that of Zn(II), the absolute concentration of gallium is in ng/mL range only. According to Copeland et al., when the concentration of Ga is large, the DPASV peaks of Ga and Zn overlap. However, in the experimental conditions adopted by us, the Ga and Zn peaks are clearly resolved.

This work reports on the use of differential pulse voltammetry in the stripping step. The deposition potential (E_d), pH and the complexing agent are important functions for the accurate determination of zinc in the presence of very high concentration of gallium.

Experimental

Voltammetric experiments were performed with Autolab PG STAT 20 (Eco-chemie, The Netherlands) coupled to a Metrohm make VA 663 stand electrode system comprising HMDE/Pt/Ag-AgCl. The PG STAT was driven by Eco-chemie software. The temperature of cell solution was maintained at 25.0±0.1°C.

All acids used were of E Merck Suprapur grade while other reagents were of analytical reagent grade. Stock solution of Zn (1 mg/mL) was prepared by dissolving ZnCl₂ in 0.1M HCl. Required standard solutions of zinc were prepared daily by diluting appropriate aliquots of the stock solution with doubly distilled deionised water. Standard solutions of various metals were added to the electrolytic cell using micropipettes with disposable tips. All glasswares were washed in 1:1 HNO₃, rinsed with deionised water, washed 3-4 times with doubly distilled deionised water before use.

Procedure

Gallium metal (150 mg) was digested in conc. HNO₃ (3ml) on a hot water bath till it dissolved and then evaporated to dryness. On cooling, the residue obtained was dissolved in citric acid. The pH of this
solution was adjusted to 4 with a few drops of ammonium hydroxide and the volume was made up to 25 ml. This solution was then transferred quantitatively to the polarographic cell, deaerated for 5 min and preconcentrated Zn(Hg), applying potential -1.10 V for 1 min. After a rest period of 15 s, a differential pulse anodic stripping voltammogram was recorded. The DPASV peak potential of Zn(Hg) was obtained at -0.972 V. Successive 0.1 ml aliquots of 5 μg/ml Zn(II) standard solutions were added to the cell and the polarograms were recorded after each addition. The peak heights and the blank current were measured and the results were calculated by the standard addition method. The results were then corrected for Zn contents of the reagent blank.

Results and discussion

Gallium is an easily hydrolysable element, hence acidic solution (pH < 2) should be used for the determination of trace impurities in gallium samples. But the masking of Zn(II) reduction peak by hydrogen ions in highly acidic solutions (pH < 2) makes it difficult to determine zinc in the gallium matrix under acidic conditions. Therefore, to estimate Zn at higher pH, a suitable complexing agent is required to suppress the hydrolysis of Ga(III) at that pH. Citric acid at pH of about 4 was thought to be a suitable labile complexing agent as it is expected to suppress the hydrolysis of gallium(III) at pH 4, and at the same time it is not that strongly complexing for zinc(II) ions to become electro-inactive. Also it is known that reduction of gallium is highly irreversible and hence shifted to much more negative potential than the standard potential (E₀ = -0.54 V vs NHE) and it is expected to shift to further negative potential than the standard potential by the addition of a complexing agent. By carefully selecting the appropriate pH, concentration of citric acid and deposition potential (Eₐ), it was possible to estimate zinc in gallium matrix by stripping voltammetry.

Differential pulse anodic stripping voltammetry of Zn (32 ng/mL) containing 6 mg/mL gallium in 0.12 M citrate buffer of various pH (4-7) (Fig. 1) was carried out keeping -1.25 V as the deposition potential and 1 min deposition time. The concentration of citric acid taken was 0.12 M, slightly in excess to that of gallium. With increase in pH, anodic current of gallium decreases so that minimum gallium interference is expected, but at the same time the difference in anodic peaks of Zn and Ga also decreases. At pH 6, a shoulder (new peak) to the gallium peak in between the peaks of Zn(II) and Ga(III) was observed, while at pH 7, a single peak was obtained at potential intermediate between that expected for Zn(II) and Ga(III). These observations might probably be due to formation of intermetallic compound between zinc and gallium. It is basically dependent on deposition potential which in-turn is a function of pH of the solution in the presence of citric acid. At pH 6 or 7, if the deposition potential is kept more positive than -1.25 V, the effect of shouldering of the peak is minimum, as a result of which, the magnitude of the DPASV current of zinc is reduced to almost nil which actually reduces the chances of intermetallic compound formation. At pH 4, separation between anodic peak potential of Zn(II) and Ga(III) was found to be maximum (Fig. 1); however the magnitude of DPASV current obtained due to Ga(Hg) was much larger than that due to Zn(Hg) and this may suppress the zinc signal. Therefore, at pH 4 the deposition potential was kept at -1.1 V instead of -1.25 V so that a reasonably high DPASV current was obtained for Zn(Hg) oxidation with minimum interference due to gallium matrix.

Differential pulse anodic stripping voltammetric calibration graph for Zn(II) (20-150 ng/mL) in the presence and absence of gallium clearly showed that Zn(II) can be determined quantitatively in the presence of gallium matrix. It was, however, observed that peak current of zinc in the gallium matrix was
about one third of that obtained in the absence of gallium. Another experiment was performed to check the effect of gallium matrix by replacing gallium matrix with aluminium matrix on molarity basis. The currents obtained in aluminium matrix were about half of that obtained in the absence of aluminium matrix. This decrease may be attributed to the viscosity effects due to gallium/aluminium salt present in the sample solutions. Aluminium has less than half the molar mass of gallium, hence the viscosity effect of same mass of aluminium is lesser. It is also possible that the decrease in the peak current of Zn in presence of gallium is due to the fact that the stripping of zinc takes place from the Hg-Ga-Zn surface, while in the absence of gallium, it is from the Hg-Zn surface. It is possible that the kinetics or diffusion characteristics or both may be different.

High purity gallium metal may contain several ultratrace impurities like lead, cadmium, copper, nickel, manganese, iron, thallium, cobalt, titanium, vanadium, aluminium etc. None of these metallic impurities interferes with the determination of Zn(II) as they are either reduced at much different potential than zinc or are electrochemically inactive as they do not form amalgam with mercury when deposition potential was kept at -1.1V for the determination of Zn.

The analysis of spiked high purity gallium metal samples was used to assess the accuracy of the proposed method because of the lack of suitable reference samples. Also the method was used satisfactorily to analyse gallium samples supplied by Novel Materials and Structural Chemistry Division of BARC and gallium oxide, 99.99% Purity (FlukaAG). The results of recovery test and sample analysis are given in Table 1.

On the basis of about 150 mg samples, Zn can be determined by the proposed procedure in gallium samples at level as low as 1μg g⁻¹ with a relative standard deviation of 14%. The sensitivity and limit of detection are essentially fixed by the rather high current of the supporting electrolyte at the peak potential. Under these experimental conditions, the blank value of Zn was found to be 4 ng mL⁻¹ with a deviation of 1ng mL⁻¹. The limit of detection was found to be 3ng mL⁻¹.

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### References


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<th>Samples</th>
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<td>0.61 ± 0.05</td>
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<th>Samples</th>
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<th>GFAAS</th>
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<td>2.4 ± 0.3</td>
<td>2.2 ± 0.4</td>
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<tr>
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<td>1.8 ± 0.2</td>
<td>2.0 ± 0.3</td>
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