

Chloride analysis in magnesium metal using ion chromatography with conductometric detection

Sangita D. Kumar^a, V.S. Tripathi^b, Niyoti Shenoy^a, B. Maiti^{a,*}

^a Analytical Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

^b Applied Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

Received 24 February 2004; received in revised form 16 June 2004; accepted 18 June 2004

Abstract

A simple, rapid and accurate method for the determination of chloride in magnesium metal has been developed. The quantitative determination of chloride was accomplished by anion exchange chromatography with conductometric determination. A Metrosep Anion Dual 2 analytical column connected in series with a Metrosep RP guard column was used for chloride separation. A solution containing a mixture of 1.3 mM Na₂CO₃ and 2 mM NaHCO₃ was used as eluent. The method requires a sample dissolution using nitric acid. The limit of detection for the determination of chloride is 50 mg kg⁻¹ and the relative standard deviation was 5% for the overall method. The recovery of chloride added was 99–102%. No interference was observed from either the closely eluting “system peak” or the nitrate peak in the determination of chloride.

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Keywords: Chloride; Inorganic anions; Magnesium

1. Introduction

Magnesium finds wide applications in industries like automobile, aerospace, nuclear reactors, etc. due to the good machinability and high corrosion resistance property of the metal and its compounds. Magnesium is also used as a reducing agent in the metallurgical extraction of different metals. It is used in Kroll's process for the production of zirconium and magnesiothermic reduction process for uranium (see [1]). Magnesium diuranate (MDU) is used as a precursor for preparing UO₂. Recently, it is also being used as a cladding material in research reactors and magnox reactors. The presence of chloride as impurity affects the physical properties of the metal and accelerates the rate of corrosion in the system by the formation of metal chlorides that hydrolyze to give hydronium ion in the system [2–4]. The hydronium ions lead to acidic environment whereby

corrosion rate increases. Hence, the determination of chloride in the magnesium metal is very important.

Several analytical methods like colorimetry [5], ion-selective electrode [6], activation analysis [7], X-ray fluorescence spectrometry [8] and ion chromatography [9,10] have been used for the analysis of chlorine in various samples. One method used to determine the chloride content in magnesium is based on the “Chloride by the gravimetric test method” contained in ASTM standard E120. This procedure assumes that all the free chloride ions react with the AgNO₃ to form AgCl. When the chloride concentration is low it is not possible to determine chloride concentration by gravimetry; hence a turbidimetric method is used [11]. Most of these methods are not suitable for the quantitative determination of chloride at trace concentration level. Hence, there is a need to develop a simple, rapid and accurate method for the determination of chloride in magnesium.

Ion chromatography with conductometric detection is considered to be a very useful instrumental technique for the simultaneous determination of ions particularly at trace

* Corresponding author. Tel.: +91 22 25595083; fax: +91 22 5505151.

E-mail address: bmaiti@apsara.barc.ernet.in (B. Maiti).

concentration level [12–14]. In the present study, it has been used for the determination of chloride in magnesium metal. The sample (magnesium metal) was dissolved in minimum volume of nitric acid and the solution was directly analyzed by ion chromatography in suppressor mode using sodium carbonate–bicarbonate mixture as eluent and conductometric method of detection.

2. Experimental

2.1. Conditions

2.1.1. Instrumentation

The ion chromatographic instrument from Metrohm (Switzerland) consisting of a 752 Pump unit, 733 IC Separation Centre, MSM Suppressor and a 732 IC conductivity detector was used for the analysis. Chloride separation was carried out in suppressor mode on a Metrosep Anion Dual-2 analytical column (75 mm × 4.6 mm) connected in series with a Metrosep RP guard column (20 mm × 4 mm). A solution containing a mixture of 1.3 mM Na₂CO₃ and 2 mM NaHCO₃ flowing at a rate of 0.8 ml min⁻¹ served as the eluent. A solution of 20 mM H₂SO₄ was used as the regenerant. The volume of the sample injection loop was 20 μL.

2.1.2. Reagents

Suprapure nitric acid (chloride 0.05 μg mL⁻¹ max) used for metal dissolution was obtained from E Merck (Germany) and all other reagents were obtained from Sarabhai M. Chemicals, India. They were of analytical grade and contained maximum of 5–10 ppm chloride. The working standard and spiking solutions were prepared by dissolving sodium salt in 18 MΩ deionized water (Barnstead, UK). Samples of magnesium metal were obtained from Uranium Extraction Division, B.A.R.C., Mumbai.

2.1.3. Sample preparation

The magnesium metal samples were cleaned by rinsing in dilute nitric acid and then dissolved using suprapure nitric acid. Sulphuric acid could also be used for the dissolution of magnesium. But nitric acid is preferred here because nitrate elutes much earlier as compared to sulphate. The concentration of chloride in the samples was determined ion chromatographically by directly injecting the sample solution into the system. However, it was necessary to control the concentration of nitrate ion in the solution in order to obtain a clearly separated peak of chloride in the presence of nitrate. Since the sample was dissolved in nitric acid, the presence of excess of nitrate overloaded the column with nitrate and a huge peak of the anion appeared in the chromatogram. It took a long time to completely elute out the nitrate. In order to avoid this difficulty, it was necessary to dissolve the sample in a minimum volume of nitric acid. The mass of the sample to be dissolved was determined by the concentration of chloride in the sample. If the chloride content of the sample was high, a smaller

mass of the sample was sufficient for obtaining a measurable peak for chloride and the dissolution could be carried out with a small amount of nitric acid. Hence, the sample mass, volume of nitric acid and concentration of chloride in the sample are all inter related. The optimum mass of the magnesium metal was determined by trial and error method. In the present set of samples, 0.5 g of the metal was found suitable. The sample was placed in a 200 mL beaker to which 20–30 mL of deionized water was added. Then, 4 mL of concentrated nitric acid was slowly added to it. The solution was diluted with deionized water to 50 mL in a volumetric flask.

2.2. Procedure

2.2.1. Ion chromatography

The sample solution prepared as described before was filtered through 0.45 μM membrane filter and diluted five times before injecting into the column. The final concentration of nitric thus reduced to 0.25 M. The sample solution (20 μL) was injected into the column and the detector response corresponding to the change in the conductance of the mobile phase was measured. The concentration of chloride was computed from the peak area. At least three separate injections were made for each analysis and the average value was taken for determination of chloride concentration.

2.2.2. Ion-selective electrode

The sample solution (10 mL) was taken in a beaker and was neutralized with dilute sodium hydroxide. To this, 10 mL of 0.1 M KNO₃ solution was added and the final volume was made up to 25 mL with deionized water. The potential of the solution was measured with an ion meter (Metrohm, Switzerland) employing chloride selective electrode (Orion) and Ag/AgCl reference electrode. The concentration of the chloride ion was calculated by comparing the observed value with a standard calibration plot.

2.2.3. Turbidity

To an aliquot (10 mL) of the sample solution, 2 mL of 2% HNO₃ and 1 mL of 2% AgNO₃ were added and mixed thoroughly and the volume was made up to 50 mL with deionized water. Turbidity due to AgCl formed was determined by measuring the absorbance of the solution at 500 nm using a spectrophotometer (Shimadzu, Japan). A calibration graph for the standards in the concentration range of 0.5–5 μg mL⁻¹ was obtained and the concentration of chloride in the sample was obtained by comparison.

3. Results and discussion

Magnesium metal is commercially produced by electrolysis of magnesium chloride. The source of chloride as impurity may originate from the starting material. The analysis of chloride in the sample solution was carried out

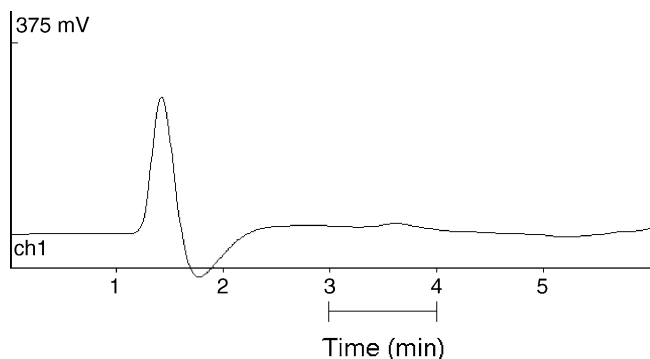


Fig. 1. Chromatogram of the blank, i.e. 0.25 M supra-pure nitric acid showing the absence of the chloride peak.

by the ion chromatographic method. A linear calibration plot $Q = 0.026A$ (where A is the area of the peak and Q the concentration in $\mu\text{g mL}^{-1}$) was obtained for standard chloride solutions in the range $0.05\text{--}10\ \mu\text{g mL}^{-1}$. The relative standard deviation evaluated from six different measurements of a chloride standard ($0.5\ \mu\text{g mL}^{-1}$) was 1.2% and the sensitivity was $0.01\ \mu\text{g mL}^{-1}$. The minimum detection limit was $0.1\ \mu\text{g mL}^{-1}$ based on 3:1 (S/N) ratio.

A chromatogram of the reagent blank (0.25 M HNO_3) was recorded in order to find out the contribution from anionic impurities if any, present in the acid (Fig. 1). There was no peak observed for chloride in the blank solution. The concentrated suprapure HNO_3 contained about $50\ \mu\text{g mL}^{-1}$ of chloride. The reagent blank containing 0.25 M acid was prepared by diluting more than 50 times the concentrated acid. Hence, the chloride concentration was too low to be detected. A typical chromatogram obtained for sample (Mg-1) is shown in Fig. 2. The dip appearing just after the chloride peak is due to the eluent anions (carbonate) and called the system peak [15]. It is seen that the chloride peak is well separated from the system peak as well as the large nitrate peak ($t_r = 6.7\ \text{min}$). The complete elution of the nitrate peak took 5 min. A small hump that appears on the tailing end of the injection peak is due to the fluoride ion in the sample solution. This was confirmed by the enhancement of the hump on spiking the sample with standard sodium fluoride

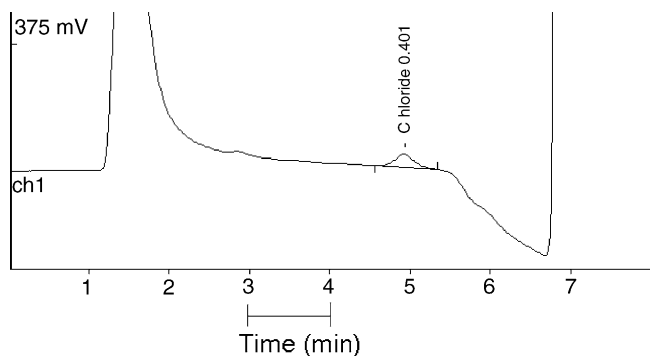


Fig. 2. Chromatogram of the magnesium metal sample (Mg-1) solution showing the chloride peak.

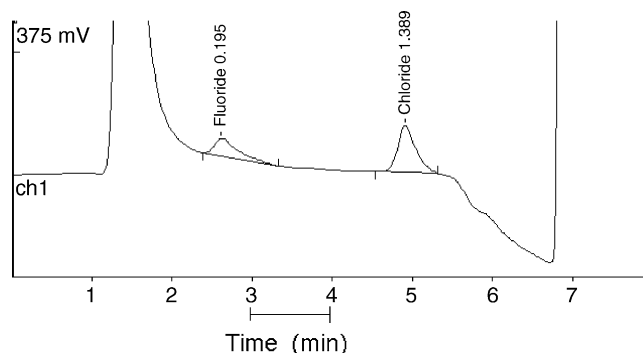


Fig. 3. Chromatogram of the magnesium metal sample (Mg-1) solution spiked with the fluoride and chloride standard solutions.

solution (Fig. 3). The large injection peak often masked the fluoride signal. In the absence of a standard reference material, identification of chloride and measurement of its concentration were performed by determination of recovery from spiked samples. The results of the recovery studies in the magnesium sample solutions spiked with different concentrations of chloride are presented in Table 1. The recoveries were in the range 99–102%. The limit of detection for chloride based on smallest quantifiable chloride peak in the sample was $50\ \text{mg kg}^{-1}$. The relative standard deviation for the chloride in magnesium metal sample, based on overall errors incorporating duplicate dissolution and replicate analysis was 5%.

Attempts were made to validate the method by measuring the chloride concentration in the samples by ion-selective electrode and turbidimetry method. The results were compared with those obtained using ion chromatography. The measurement of chloride ion concentration using chloride ion-selective electrode was not successful because of serious interference from the matrix elements. In normal practice, masking the cations with buffers containing amino polycarboxylic acids eliminates the interferences from cations during the measurement of anion concentrations. In the present

Table 1
Recovery of chloride from different samples

Sample	Chloride sought ($\mu\text{g mL}^{-1}$)	Chloride found ($\mu\text{g mL}^{-1}$)	Recovery (%)
Mg-1	0.5	0.51	102
Mg-1	1.0	0.988	98.8
Mg-2	1.5	1.53	101

Table 2
Determination of chloride in different magnesium metal samples

Sample	Concentration	
	Ion chromatography (mg kg^{-1})	Turbidimetric method (mg kg^{-1})
Mg-1	200 ± 10	186 ± 14
Mg-2	447 ± 22	440 ± 35
Mg-3	466 ± 23	460 ± 37
Mg-4	496 ± 25	510 ± 40

study, the masking agents did not yield satisfactory results because the measurements were carried out in neutral solutions. It was not possible to mask magnesium with the reagents at the neutral pH region. Magnesium forms complex with the amino polycarboxylic acids only at $\text{pH} > 8$. The measurement of Cl^- by ion-selective electrode could not be carried out at higher pH due to interference from OH^- ion. In turbidimetry, the results obtained were corrected for the reagent blank and the values obtained by both the methods are in good agreement as shown in Table 2.

4. Conclusions

Both the stages of the method involving acid dissolution and analysis are relatively simple, inexpensive and rapid using readily available chemicals and equipment. The use of ion chromatography detection allows the simultaneous separation and detection of chlorine in contrast to ion-selective electrode or turbidity method. The method gives good agreement with the values obtained by turbidimetry method. Reasonably accurate and precise spike recoveries for chlorine were obtained.

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