Spectrophotometric Determination of Chromium (VI) in Nitric Acid by Means of Solvent Extraction with Molten Mixtures of Naphthalene and Biphenyl

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Abstract

A method for the Spectrophotometric determination of chromium (VI) after extraction of its ternary complex with ammonium pyrrolidinedithiocarbamate (APDC) as the chelating agent in to molten naphthalene – biphenyl has been developed. The Cr-(PDC)3 complex in a nitric acid solution is quantitatively extracted from into molten naphthalene – biphenyl at about 70 ºC. Organic phase can be obtained as a solid lump on the surface of the aqueous phase, making its collection simple. Therefore the organic phase dissolved in methyl isobutyl ketone (MIBK). The chromium in this solution is than determined by using atomic absorption technique. The effect of different variables such as acid concentration, naphthalene– biphenyl, shaking time, foreign ions and APDC concentration was investigated.

Keywords: chromium (VI), determination, extraction, APDC, naphthalene – biphenyl

1. Introduction

Chromium is one of the most abundant elements on Earth. The amount of chromium in the environment has gradually been increased predominantly by industrial activities especially from tanneries, mines and
incinerators [1]. Chromium is usually found in natural media as hydrated chromium (III) species or as chromium (VI) (chromate) [2].

The last has a definitely toxic impact on living organisms and humans, with mutagenic and potential carcinogenic properties [3]. Due to the constant interest for toxic elements monitoring, extended reviews about the analytical methodologies applied to chromium determination are recently published for liquid and solid matrices [4–6].

A direct measurement of chromium species is not feasible with atomic absorption spectrometry and other atomic spectroscopic techniques. There are only a few analytical techniques available that have sufficient sensitivity and selectivity for the direct determination and speciation of trace levels of chromium in environmental samples [1,7,8,9]. Separation of chromium species using various separation–preconcentration procedures including liquid–liquid extraction, solid phase extraction, coprecipitation, etc. combined with flame and/or graphite furnace atomic absorption spectrometry often results in inadequate sensitivity for trace concentrations of chromium in real samples [7,10–13].

Although ammonium pyrrolidinedithiocarbamate (APDC) has been used recently in various preconcentration and separation techniques, [14-19] APDC is most widely used to determine the metal ions that form slightly soluble complexes in an aqueous solution.[20] Dithiocarbamate complexes are more stable in acid solutions and can be successfully used as reagent for the extraction of several metals in liquid-liquid extraction techniques [21–23]. Recently, using solid metal dithiocarbamate, a new solid-phase extraction method has been described for the determination of copper, cadmium and nickel by FAAS [24–25].

![Molecular structure of ammonium pyrrolidinedithiocarbamate (APDC)](image)

Fig. 1. Molecular structure of ammonium pyrrolidinedithiocarbamate (APDC)

The aim of the presented work is to establish a speciation procedure based on adsorption of Cr (VI) - PDC chelates on molten mixture of naphthalene – biphenyl for hexavalent chromium samples.

2. Experimental

2.1. Reagents

All reagents were of analytical reagent grade. Standard chromium (VI) solution 5ppm was prepared by dissolving 0.01414g of potassium dichromate in demineralised water and diluting to 200 cm3. Stock solutions of other metals were prepared by dissolving appropriate amounts of the metal salts. Nitric acid 0.01M, 0.05M, 0.1M, 0.5M and 1M was prepared by dissolving 0.0833, 0.416, 0.833, 4.16 and 8.33cm3 respectively. Ammonium pyrrolidinedithiocarbamate (APDC) was prepared by dissolving 0.1g in 100 ml Deionized water.

2.2. Equipment

A Hitachi, Model 180-30 atomic absorption spectrophotometer, was used for determination of chromium. An air-acetylene flame with a flow rate of 3 mL/min for acetylene and 10 mL/min for air was used for atomic absorption spectrophotometry and the chromium estimation was carried out at 357.9 nm
2.3. General Procedure

Transfer 20 cm³ solution contain 5 μg/mL of Cr⁶⁺ in to 100 cm³ Erlenmyer flask, add 10 cm³ of 0.1% APDC, 10 cm³ of nitric acid and 400 mg of mixture of naphthalene – biphenyl (3:1). Heat the flask on a water- bath at about 70 °C until the naphthalene – biphenyl phase melts completely, then shakes it vigorously for 1 min, cool the mixture rapidly while stirring, separate naphthalene – biphenyl containing the metal complex by filtration through a filter paper, dry it on a filter paper and dissolve it in methyl isobutyl ketone.

3. Results and Discussion

3.1. Effect of acidity

The effect of acidity on the extraction of the complex was studied with sample containing 5ppm of chromium (VI), keeping the other conditions constant. Fig. 2 showed that the extraction of complex is dependent on acid concentration (pH), the maximum extraction obtained at 0.1 M nitric acid, so a 0.1 M was chosen all subsequent measurements.

![Fig. 2. Effect of nitric acid concentration on extraction](image)

3.2. Effect of addition of naphthalene – biphenyl

The amount of naphthalene – biphenyl were varied from 0.2 to 1.0g and the extractions were carried out by the general procedure. The extraction was quantitative in this range, but above 1.0g it was difficult to dissolve the naphthalene in limited amount of methyl isobutyl ketone. Hence 0.4g of naphthalene – biphenyl was used as the most suitable amount. The best percentage of naphthalene / biphenyl was 3:1. Fig. 3 showed that the extraction of complex is dependent on amount of naphthalene – biphenyl.

3.3. Effect of APDC concentration

The volume of the reagent was varied, with the other conditions being kept constant. The extraction
percentage remained constant with the use of 10 cm³ of 0.1% APDC solution in both instances.

3.4. Effect of shaking time

The extraction of the complex into molten naphthalene – biphenyl was found to be very rapid and no change was observed when the shaking time was varied from 20 to 240 s.

![Graph showing extraction percentage vs amount of naphthalene-biphenyl](image)

Fig. 3. Effect of amount of naphthalene – biphenyl on the extraction

Table 1. Effect of some foreign ions on the recoveries of Cr(VI) (N=3)

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Concentration (µg mL⁻¹)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>10000</td>
<td>95 ± 3</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>2000</td>
<td>95 ± 3</td>
</tr>
<tr>
<td>K⁺</td>
<td>6000</td>
<td>96 ± 2</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>2000</td>
<td>95 ± 3</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>10000</td>
<td>95 ± 3</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>50</td>
<td>95 ± 3</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>50</td>
<td>96 ± 2</td>
</tr>
</tbody>
</table>

3.5. Effect of foreign ions

The effect of foreign ions which interfere with the determination of analytes by the presented method or often accompany them was examined with the optimized conditions to assess the possible applications of the procedure. Various salts and metal ions were added individually to a solution containing Cr(VI) and the test procedure was applied. The recoveries of analytes were higher than 95%. Tolerable limit was defined as the highest amount of foreign ions that produced an error not exceeding 5% in the determination of investigated analyte ions by the combination of presented procedure and the flame atomic absorption spectrometric
determination methods. The results are summarized in Table 1. As it is seen, large numbers of ions used have no considerable effect on the determination of analyte ions.

3.6. Limit of detection and qualification

The limit of detection (LOD) and limit of qualification (LOQ) of the present work were calculated under optimal experimental conditions. The limit of detection for chromium (VI) based on three times the standard deviations of the blank (N= 11) was 0.002 μgL⁻¹. Limit of qualification (LOQ) value was found as 0.0067 μgL⁻¹.

4. Conclusion

An effective spectrophotometric determination of chromium (VI) with ammonium pyrrolidinedithiocarbamate (APDC) using molten mixture of naphthalene - biphenyl has been established. The proposed method proved to be accurate and applicable to chromium determination in a variety of sediments and water samples.

References