



Spectrofluorometric determination and chemical speciation of trace concentrations of chromium (III & VI) species in water using the ion pairing reagent tetraphenyl-phosphonium bromide

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ABSTRACT

A highly selective, and low cost extractive spectrofluorometric method has been developed for determination of trace concentrations of chromium (III & VI) in water samples using the fluorescent reagent tetraphenylphosphonium bromide (TPP⁺·Br⁻). The method was based upon solvent extraction of the produced ion associate [TPP⁺·CrO₃Cl⁻] of TPP⁺·Br⁻ and halochromate in aqueous HCl and measuring the fluorescence quenching of TPP⁺·Br⁻ in chloroform at $\lambda_{ex/em} = 242/305$ nm. The fluorescence intensity of TPP⁺·Br⁻ decreased linearly on increasing the chromium (VI) concentration in the range of 1–114 $\mu\text{g L}^{-1}$. The limits of detection (LOD) and quantification (LOQ) of chromium (VI) were 0.43 and 1.42 $\mu\text{g L}^{-1}$, respectively. Chromium (III) species after oxidation to chromium (VI) with H₂O₂ in alkaline solution were also determined. Chemical speciation of chromium (III & VI) species at trace levels was achieved. The method was applied for analysis of chromium in certified reference material (IAEA Soil-7) and in tap- and wastewater samples and compared successfully (>95%) with the inductively coupled plasma-mass spectrometry (ICP-MS) results.

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1. Introduction

Chromium occurs in the environment in two major valence states (III, VI). Due to its wide use in electroplating, leather tanning, metal finishing, nuclear power plant, textile industries, and chromate preparation, chromium (VI) exists in air, soil, and aquatic systems [1]. It can also enter the drinking water distribution system from the corrosion inhibitors used in the water pipes [2]. Although the trivalent form is an essential nutrient, its disposal as liquid effluents in natural waters or as sludge in soils has to be avoided or controlled, because it may be oxidized, especially in soils, to the hexavalent form, which is highly toxic, carcinogenic and mutagenic in nature [3]. The ability of chromium (VI) to react with other elements and its high solubility in soil and aquatic systems makes it more toxic than other heavy metal ions [4,5]. Thus, total chromium measurement cannot be used to determine the actual environmental impact and chromium (III, VI) speciation in the environmental

samples is necessary to assess precisely the pollution levels [5].

The presence of chromium (VI) in the environment has resulted in the development of numerous analytical techniques for its preconcentration by solid phase extraction [6,7] and subsequent determination in different sample matrices. The most common analytical techniques for chromium determination are flow injection analysis [8], inductively coupled plasma mass spectrometry (ICP-MS) [9], graphite furnace atomic absorption spectrometry (GFAAS) [10] and adsorptive stripping voltammetry [11]. The main disadvantages of these techniques are the complexity and the high cost of the instruments, and the need of some degree of expertise for their proper operation. Therefore, the development of low cost method, easy to operate, highly sensitive and reliable for routine analysis e.g. spectrofluorimetry or spectrophotometry is still of great concern. The former technique is better than the later due to its high sensitivity and selectivity.

Recently, the complex ion associate of the halochromate (CrO₃Cl⁻) and the ion pairing reagent tetraphenylphosphonium bromide (TPP⁺·Br⁻) in chloroform has been used for the development of a simple and accurate extractive spectrophotometric procedure for speciation of chromium (III, VI) species in water [5]. Recent literature revealed no study on the use of the fluo-

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