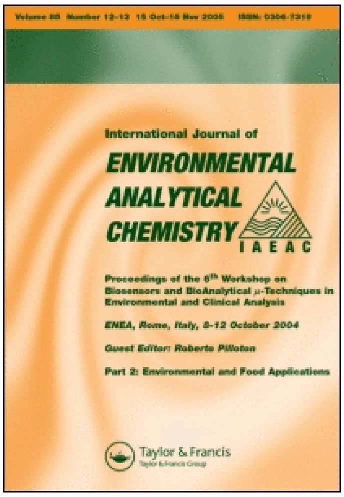

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Trace Analysis of Titanium in Environmental Samples using *N-p*-Methoxyphenyl-2-Furohydroxamic Acid for Separation and Colorimetric Determination

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Trace Analysis of Titanium in Environmental Samples using *N-p*-Methoxyphenyl-2-Furohydroxamic Acid for Separation and Colorimetric Determination

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A separation-spectrophotometric method employing *N-p*-methoxyphenyl-2-furohydroxamic acid (MFHA) for the trace analysis of titanium (IV) is presented as the most sensitive and selective of all reported methods employing hydroxamic acids for the purpose. Titanium was determined in plants, soils, water and steels, with a sensitivity of 0.007 ppm.

KEY WORDS: Titanium, environmental samples, separation, determination, trace analysis

INTRODUCTION

Titanium resembles aluminium in being extremely abundant in the lithosphere and in soils and in being poorly absorbed and retained by plants and animals.[1] Over 50 years ago, investigators examined a wide variety of plants for titanium and recorded levels ranging from 0.1 to 5 ppm, with a high proportion of the values lying close to 1 ppm. Very similar concentrations were reported by Mitchell[3] in his later study of the mineral composition of red clover and ryegrass grown on different soils. Very little is known of the titanium content of human foods. Tipton *et al.*[4] reported the 30 day mean total dietary titanium intakes of two individuals to be 0.37 and 0.41 mg/day. A surprising feature of this investigation was the high urinary excretion, suggesting either considerable absorption from the diet or loss from previously retained tissue titanium. Both individuals were in substantial negative titanium balance, with approximately equal excretion via the feces and the urine.

Bertrand and Varonea-Spirit[2] determined the titanium content of the tissues of a number of animals and marine organisms with highly variable results. In the domestic animals the highest concentration (2 ppm of dry tissue) was found in the liver. Tipton and Cook[4] also found great variability in the levels of titanium in all adult human organs examined, with some samples of tissue below the limit of detection of the method, namely 0.2 ppm of dry tissue. Most of the soft tissues contained 0.3–0.6 ppm but the lungs averaged over 20 ppm, with some samples containing over 250 ppm. Evidence was obtained that titanium accumulates with age in the lungs, but not in the liver and kidneys. A high proportion of the titanium in the lungs, like the aluminium and the silicon, presumably comes from the inhalation of atmospheric dust.

The levels of titanium in environmental samples are evidently low and a sensitive method is essential for its determination.

N-*p*-Methoxyphenyl-2-furohydroxamic acid (MFHA) was recently introduced as a new reagent for vanadium (V).[5] When explored for titanium (IV), MFHA proved equally effective. It was found that traces of titanium (IV) are completely extracted with 5 + 2 minutes of equilibration with a 1 M solution of MFHA in chloroform from aqueous solutions containing 10–12 M HCl. The interference from iron, molybdenum, chromium, zirconium and tantalum can be eliminated by carrying out extractions in presence of 0.2–0.4 M stannous chloride. The golden-yellow Ti (IV)-MFHA extract has maximum absorbance at 385 nm ($\varepsilon = 7.1 \times 10^3$ Litre mole^{-1} cm^{-1}) and obeys Beer's Law in the range 0.5–10 ppm of Ti (IV). The method is more sensitive and selective than other methods employing hydroxamic acids[6,7] and is suitable for the determination of titanium in plants, soils, water, and steels.

EXPERIMENTAL

MFHA was synthesised and purified as described previously.[3] A 1 M solution of the reagent in ethanol-free chloroform was employed for extraction work. The titanium (IV) solution was prepared in deionised water and standardised.[8]

EXTRACTION PROCEDURE

An aliquot, containing 5–50 ppm of Ti (IV) in 10–12 M HCl, was transferred into a separating funnel followed with 2 ml of 5 M $SnCl_2$

solution (prepared in 10 M HCl), and 10 ml of a 1 M solution of MFHA (in chloroform). The contents were equilibrated for 5 minutes, the phases were allowed to settle, and the chloroform extract was separated. The extraction was repeated for two minutes, and the mother liquour was washed with two 2 ml portions of chloroformic reagent solution to recover any trapped droplets of the extract. The extracts and the washings were combined, and diluted to 25 ml with chloroformic reagent solution. The absorbance of the extract was measured at 385 nm against the reagent solution as blank. A calibration curve was set accordingly.

RESULTS AND DISCUSSION

Absorption spectra

The Ti (IV)-MFHA system shows maximum absorbance at 385 nm. (Figure 1). The reagent has negligible absorbance in this region.

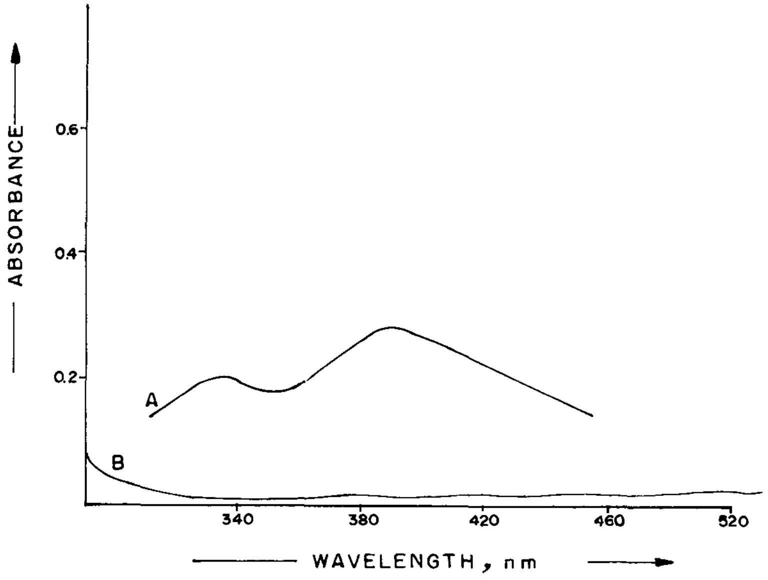

FIGURE 1. Absorption spectra of (A) titanium MFHA system (Ti, 0.41×10^4 M; MFHA, 1.0 M) and (B) MFHA.

Beer's Law, molar absorptivity, sensitivity and reproducibility

Beer's Law was obeyed over the range 0.5–10 μg/ml of titanium (IV), the molar absorptivity being 7.1×10^3 l mole^{-1} cm^{-1}. The sensitivity of the method, as per Sandell's definition[9] was 0.007 $\mu g/cm^3$ of titanium (IV). The reproducibility of the method was checked by replicate analysis of titanium solutions. Six determinations, each with 5 $\mu g/ml$ and 50 $\mu g/ml$ titanium (IV) solutions, yielded standard deviation values of ±0.07 and ±0.09 respectively.

Effect of thiocyanate ion

The colour of the extract was enhanced ($\varepsilon = 1.25 \times 10^4$ l mole^{-1} cm^{-1}) if extractions were done in presence of 0.01 M thiocyanate but there is a loss in selectivity as several ions, especially iron, begin to interfere seriously.

Effect of diverse ions

In presence of 0.2–0.4 M $SnCl_2$ and in absence of thiocyanate concentrations higher than the molar ratio 10:1 :: thiocyanate : Ti (IV), the present method tolerated alkali metals and alkaline earth metals when present in molar ratios 100:1 :: foreign ion : Ti (IV). Cu (II), Co (II), Zn (II), Hg (II), Ag (I), Cd (II), Uo_2 (II), V (IV), Fe (II) Fe (III), Al (III), La (III), Sc (III), Ga (III) and Th (IV) were tolerated when present in 50 fold the amount of Ti(IV). No interference was encountered from halides. acetate, carbonate, nitrate and oxalate, Cr (VI) and Mo (VI), were tolerated up to 10:1 :: foreign ion : Ti(IV) while a 5-fold excess of Zr (IV), and Ta (IV) had no effect on the determinations. Niobium was tolerated if not present in more than equimolar concentrations with Ti (IV).

Stoichiometry of the titanium-MFHA complex

The modified Job's method of continuous variation[12] and the molar ratio method[13] were applied to study the stoichiometry of the complex. The molar ratio method (Figure 2) did not yield a plot with a sharp break at 2 mol of MFHA per mol of Ti (IV) but results obtained by extrapolation indicate a 2:1 :: MFHA : Ti (IV) system. The Job's curve (Figure 3) also indicates a complex of the same stoichiometry.

Analysis of titanium in steel

The analysis of a steel sample from the National Bureau of Standards, USA, was carried out to check the reliability of the present method. Six determinations with the sample NBS 170 A gave value 0.282 ± 0.002 % for titanium (Standard value 0.28 %).

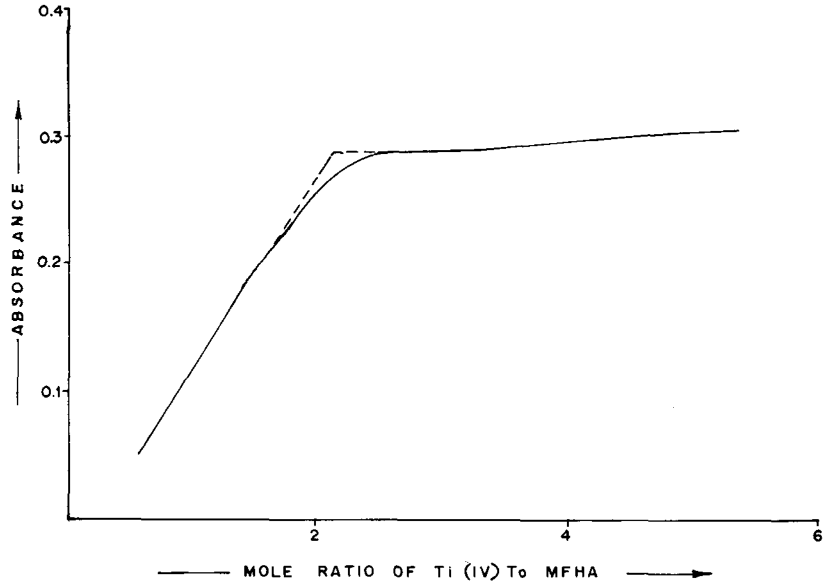

FIGURE 2 Mole ratio curve.

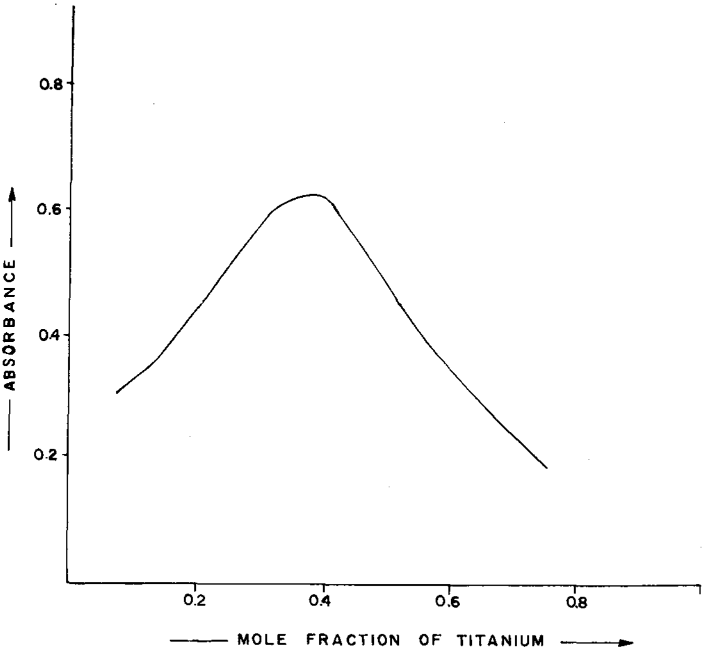

FIGURE 3 Job's plot for continuous variation.

Analysis of titanium in plants, soils and water

The plant and soil samples were collected and brought into solution by ashing (for plants), alkali fusion (for soil), and acid treatment as per standard procedures.[10] The water samples were acidified to pH $\simeq 0$ with HNO_3, boiled for $\simeq 5$ minutes and filtered through a 0.45 mu membrane filter. The acidity of each sample was then adjusted to 10–12 M HCl and the extraction and analysis of titanium was carried out as described above. The results are presented in Table I.

TABLE I
Analysis of plants, soils, and water

Sample	Titanium present[a]	Titanium added	Titanium found (six determinations)
Fodder plant			
(*Melilotus indica*)	0.0 ppm	5.0 ppm	5 ± 0.04 ppm
(*Melilotus indica*)	0.0 ppm	20.0 ppm	20 ± 0.05 ppm
Grass			
(*Chloria Barbata*)	0.0 ppm	10.0 ppm	10 ± 0.007 ppm
Soil I	61.5 ppm	0.0 ppm	61 ± 0.9 ppm
Soil II	61.5 ppm	50.0 ppm	111 ± 1.4 ppm
Pond water I	0.0 ppm	5.0 ppm	5 ± 0.06 ppm
Pond water II	0.0 ppm	25.0 ppm	25 ± 0.11 ppm

[a] Determined by atomic absorption spectrometry.[11]

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