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Spectrophotometric determination of vanadium in crude oil

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Abstract

Spectrophotometric method has been developed for the determination of vanadium after derivatization with 2-pyrrolealdehyde phenylsemicarbazone (PPS). The linear calibration curve was obtained with 2.5–20 μg/ml vanadium. Copper(II), cobalt(II), iron(II) and palladium(II) could also be determined separately using PPS with linear calibration curves within 2.5–12.5, 5–15, 2.5–15 and 1–5 μg/ml at 362, 355, 355 and 365 nm, respectively. The vanadium in crude oil was determined with relative deviation (RSD) of 2.5–5.0%. The methods have been applied for the analysis of copper from copper wires, cobalt from pharmaceutical preparation and palladium from palladium on barium sulphate with RSD within 2.6–4.5%.

Keywords: Crude oil; Vanadium; Petroleum; Sindh; Bioelements; Indus basin; Pakistan

1. Introduction

Vanadium is a bioelement which is used in various enzymes such as haloperoxidases, nitrogenases and inhibitory towards phosphatases processes [1,2]. Some of the vanadium compounds stimulate glucose uptake and inhibit lipid breakdown in a manner remarkably reminiscent of insulin effects [3]. Vanadium containing haloperoxidases catalyzes the oxidation of halides in the presence of hydrogen peroxide to a highly reactive intermediate, i.e. hypohalous acid, which reacts with suitable nucleophilic acceptor, if present, forming a halogenated compound [4,5] and with hydrogen peroxide yielding H_2O [5,6]. It has been established that vanadium peroxidases are able to catalyze the oxidation of organic sulfides to the corresponding sulfoxides in the presence of hydrogen peroxide [7–10]. Heavy crude petroleum oils contain vanadium, nickel, iron, and copper as organically bound metals, mostly as metalloporphyrins and metallo-non-porphyrins [11,12]. Their determination is of considerable importance because the metal complexes are poisonous and foul catalysts or cause undesirable side reactions in refinery operations such as fluid cracking and hydrodesulfurization [13]. A number of analytical methods have been used for the determination of metal ions in crude petroleum oils, including atomic absorption spectrometry (AAS) [14], inductively coupled plasma atomic emission spectroscopy (ICPAES) [15], radioisotope X-ray fluorescence [16], neutron activation [17] and gas

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chromatography (GC) [18]. Semicarbazones and their metal complexes are well known to be biologically important and interesting because of their anticarcinogenic, antibacterial, and antifungal properties [19,20]. They have been screened for their medicinal properties because they possess some degree of cytotoxic activity [21]. The biological activity of certain semicarbazones is due to their ability to form chelates with transition metal ions [22]. As common ligands, semicarbazones are easy and cheaper to synthesize. They dissolve easily in solvent and their solutions are stable for more than 24 h. In addition, they are widely used in metal analysis due to their ability to form metal complexes [23,24]. The present work examines the potential of the reagent pyrrolealdehyde phenylsemicarbazone (PPS) for the spectrophotometric determination of vanadium in crude oil.

2. Experiment

Equipments: Spectrophotometric studies were carried out on Hitachi 220 Spectrophotometer with 150 W deuterium lamp and 1.0 quartz cuvette. Varion AA 220 atomic absorption spectrometer and Orion 420A pH meter with combined 8102 SC electrode were used.

The elemental microanalysis was carried out by Elemental microanalysis, Devon, England.

GR grade chemicals—sodium acetate, acetic acid, sodium bicarbonate, sodium carbonate, boric acid, borax, ammonium chloride, ammonia, chloroform, acetonitrile, hydrochloric acid (37%) (E. Merck), palladium(II)chloride, nickel(II)chloride, copper(II)chloride, 2-pyrrolealdehyde and phenylsemicarbazide (Fluka)—were used. Freshly prepared doubly distilled water for all glass was used throughout the work. The buffer solutions in the pH range 1–10 at unit interval were prepared from potassium chloride(1 M)–hydrochloric acid pH 1–2; sodium acetate(1 M)–acetic acid (1 M) pH 3–6; ammonium acetate(1 M)–acetic acid (1 M) pH 7; boric acid(1M)–borax(1 M) pH 8–9; and ammonium chloride(1 M)–ammonia pH 10.

All glasses were previously soaked in 10% nitric acid for 24 h and rinsed with double distilled water before use.

Preparation of 2-pyrrolealdehyde phenylsemicarbazone (*PPS*): The PPS was prepared by condensation of 2-pyrrolealdehyde (1.0 g) dissolved in methanol (20 ml) with phenylsemicarbazide (1.5 g) in methanol (30 ml) in the presence of acetic acid (2 ml). The contents were refluxed for 2 h, concentrated to about 20 ml and cooled at 5 °C overnight. The precipitate obtained (yellowish) was filtered and recrystallized from ethanol and melting point was noted as 186 °C.

2.1. Solvent extraction

To an aliquot of solution (1–2 ml) in 10-ml flasks containing 25–200 μg of vanadium(IV) or 25–125 μg of palladium(II) and copper(II), or 50–150 μg of cobalt(II) and iron(II) separately was added reagent solution (PPS) of 2–4 ml (0.2% w/v in ethanol). The solution was added to 2 ml of appropriate buffer solution and the mixture was heated on water bath for 5–15 min at 70–75 °C. The contents were allowed to cool and were transferred to a separating funnel. Chloroform (3 ml) was added and the contents were mixed well. The organic layer was separated and the extract was transferred to 10-ml flask. The extraction was repeated with 3 ml of chloroform. The volume was adjusted up to 10 ml with chloroform added to 1 ml absolute ethanol. The absorption spectra of metal chelates against reagent blank were recorded on Hitachi 220 spectrophotometer.

2.2. Analysis of copper from copper wires

Copper wire of 0.5 g was dissolved in aqua regia (8 ml) and was heated near to dryness. The residue was dissolved in 3–4 ml hydrochloric acid (37%) and again heated near to dryness. The residue was dissolved in 3 ml of water and the volume was adjusted up to 100 ml with double distilled water. The solution of 5 ml was further diluted to 50 ml and 1 ml of the solution was used and procedure as in Section 2.1 was followed. The absorbance was measured at 362 nm against reagent blank and the amount of copper from copper wires was calculated from calibration curve.