

A new reagent system for the highly sensitive spectrophotometric determination of selenium

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Abstract: Highly sensitive and simple spectrophotometric determination of selenium is described for the determination of selenium(IV) using a new reagent leuco malachite green. The method is based on the reaction of selenium(IV) with potassium iodide in an acidic condition to liberate iodine, the liberated iodine oxidizes leuco malachite green to malachite green dye. The green coloration was developed in an acetate buffer (pH 4.2 – 4.9) on heating in a water bath (~ 40 °C). The formed dye exhibits an absorption maximum at 615 nm. The method obeys Beer's law over a concentration range of 0.04 – 0.4 $\mu\text{g mL}^{-1}$ selenium. The molar absorptivity and Sandell's sensitivity of the color system were found to be $1.67 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ and 0.5 ng cm^{-2} , respectively. The optimum reaction conditions and other analytical parameters have been evaluated. The proposed procedure has been successfully applied to the determination of selenium in real samples of water, soil, plant material, human hair, and cosmetic samples. The results were compared to those obtained with the reference method. Statistical analysis of the results confirms the precision and accuracy of the proposed method. In addition, the developed method is cost-effective and involves easily accessible instrumentation technique which can be used by ordinary research laboratories.

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1 Introduction

Selenium is an indispensable element associated with all living beings. It is reported to be toxic as well as an essential trace element, because it acts as a cofactor in cell membrane glutathione peroxidase and is important in cellular detoxification of peroxides [1–3]. The

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major sources of selenium in the environment are volcanic eruption, insecticides, fertilizers, smelting ceramics, metallurgical operation, glass rubber accelerators, paints, dyes and electronic goods. Certain industrial and agricultural processes release selenium as a by-product, and there are cases where selenium from such sources has caused environmental disasters [4, 5]. Selenium is also reported to be present in cigarette paper, tobacco [6], and various cosmetic samples [7]. Selenium enters into natural water through seepage from seleniferous soil and industrial waste. Water drained from such soil may cause severe environmental pollution and wild life toxicity [8]. According to the sanitary and hygiene standards, the maximum permissible concentration of selenium in water is 0.05 mg L^{-1} [9]. The threshold limit value (TLV) for selenium compounds in air is $0.1\text{--}0.2 \text{ mg dm}^{-3}$ [3]. An excess of selenium ($> 5 \text{ mg}$) in the human body can cause poisoning [10].

After initial concerns regarding the selenium toxicity, many studies have focused on its nutritional importance, metabolic function and the aspects related to deficiency in animals and humans. The association between low nutritional selenium status and increased risks of cardiovascular disease, carcinogenesis and the role of selenium supplementation in the prevention and treatment of AIDS – related pathology has been considered in many epidemiological studies [11–13]. As a cofactor of glutathione peroxidase, selenium is involved in the activity of the immune system [14]. Selenium is incorporated in the active center of antioxidant selenoenzymes. Owing to these antioxidative properties, which prevent oxidative damage to DNA and other important biomolecules, selenium may prevent cancer [15]. In China, selenium deficiency in the soil is associated with Keshan disease and Kaschin Beck disease [16, 17].

The toxicity, availability and environmental mobility of selenium are very much dependent on its chemical forms [18]. In many environmental matrixes, e.g. natural water and soils, the predominant oxidation states of selenium are Se(IV) and Se(VI). Precise knowledge of the amounts of selenium and its compounds present in a system is therefore required for accurate assessment of the environmental and biological impact of selenium. This has resulted in an increasing need for analytical methods suitable for their determination at trace levels.

Various instrumental techniques: HG-ICP-MS [19], HPLC-ICP-MS [20], HPLC-UV-HG-AES [21], ICP-OES [22], NAA [23], AAS [24], stripping voltammetry [25], flow injection spectrophotometry [26], etc. are available in the literature for the determination or speciation of selenium including spectrophotometry. Except spectrophotometry, most of the other methods are disadvantageous in terms of cost and instruments used in routine analysis. Several spectrophotometric methods have been reported for the determination of selenium. Marczenko has reviewed the reported spectrophotometric methods for the determination of selenium up to 1986 [27]. Irena Nemcova *et al.* have discussed the reagents used and reactions involved in the determination [28], which includes chromogenic reagents, ion-associates, Postowsky reaction, etc. Recently, formation of ion-associate with the liberated iodine from the oxidation of iodide by selenium [29], starch-iodine [30], bleaching of the dye thionin [31] and a kinetic spectrophotometric method [32] have been reported for the determination of selenium. Many of the reported meth-