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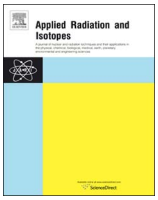

Multi-element detection in sea water using preconcentration procedure and EDXRF technique

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HIGHLIGHTS

- EDXRF Method was used to detect 11 trace elements in sea water.
- Pre concentration of trace elements done using APDC and MIBK.
- Secondary targets and filters used for the EDXRF analysis.
- The method was validated with ICP AES technique.

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ABSTRACT

A method was optimized for detecting trace elements in sea water using Energy dispersive X-ray fluorescence (EDXRF) technique. Sea water samples were pre-concentrated using ammonium pyrrolidinedithiocarbamate (APDC) as chelating agent and methyl isobutyl ketone (MIBK) as organic phase. The preconcentrated samples were dried to form thin films on mylar substrate and analysed using EDXRF spectrometer. The multi-element standard samples prepared in synthetic sea water were used for EDXRF instrument calibration. The instrument was calibrated for 11 elements namely As, Cd, Co, Cr, Fe, Ga, Pb, Se, Sc, V and Zn using linear regression method for concentration up to 200 ppb. The detection limits achieved for As, Cd, Co, Cr, Fe, Ga, Pb, Se, Sc, V and Zn were 13, 70, 5.1, 36, 15, 36, 23, 11, 20, 13 and 40 ppb respectively. The optimized method was used for determination of elements in sea water collected from the Thane creek, Mumbai, India. The results were checked for accuracy by comparing it with inductively coupled plasma atomic emission spectroscopy (ICP AES) technique. The comparison showed the discrepancy of results to be insignificant at 95% confidence level.

1. Introduction

The dissolved constituents of sea water can be mainly grouped as major or conservative and the trace components. The time required for concentration changes of the conservative constituents is very long, since they are not influenced significantly due to biological, chemical and geochemical processes. Therefore, their distribution is controlled mainly by the physical processes of advection and convection, turbulence diffusion, etc. (Brügmann and Kremling, 1999). The trace constituents, in addition to being affected by physical processes, are also influenced by the biological processes of uptake, excretion and biodegradation. In general, the concentrations of trace elements in sea water are extremely low, but often reflect some changes in the aquatic environment due to biological activities or environmental pollution from artificial sources. Their release in aquatic ecosystem is triggered by both natural and anthropogenic processes (Zhang et al., 2009). Consequently monitoring of trace elements in coastal and open sea waters becomes important for environmental conservation. Traditionally, trace elements in sea water are determined with well established analytical techniques which include ICP MS, ICP AES, AAS, voltammetric techniques, and NAA (Butcher, 2010; Herzog and Beni, 2013; Beck et al., 2002; Søndergaard et al., 2015; Wang and Hansen, 2005; Greenberg et al., 2011). These techniques provide reliable results and detection limits going down to ppt levels. The procedures for using these techniques though extremely accurate and precise, requires lot of time and skill in sample processing.

The XRF technique has emerged as an alternative providing less accurate but fast analysis for sea water elemental determination (Margui, 2014; Pashkova and Revenko, 2015). The XRF measurements suffer from inter elemental interferences and matrix effects. It requires

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matrix matched standards for calibration. Total-XRF and EDXRF are proven to provide detection limit as low as ppb in water samples (Margui et al., 2014; Van Grieken and Markowicz, 2001). Such a technique can be quite useful when sea water samples needs to be analysed more often than not. The XRF analysis of liquid samples can be done by placing a few milliter (mL) of liquid in thin film bottomed cup. The liquid samples being homogeneous give analytical result representative of the whole sample. However, high X-ray background scatter makes it difficult to quantify elements at such low concentration. The salt content of sea water can lead to formation of crystals and subsequent decrease in signal-to-noise ratio. The direct analysis of liquid samples in XRF set up generally provides detection limits in the ppm range (Margui et al., 2014). The detection limits can be improved by using sample pre treatment or pre concentration methods prior to X-Ray analysis. The solid thin homogenous targets formed from pre concentration procedures are ideal for use in combination with XRF. Most of the pre concentration methods are based on precipitation and solid liquid extraction (Marguí et al., 2010; Margui et al., 2014). The precipitation method is based on the addition of a precipitating agent to the solution and the determination of the target elements in the solid obtained after a filtration procedure. The solid liquid extraction involves use of solid sorbents and activated thin layers (Abe et al., 2006; Pyrzynska, 2010; Sitko et al., 2006). The recent advances in XRF technology, the use of source modifiers (primary filters and secondary targets) and the new generation of compact, solid-sate detectors (PIN diodes and silicon-drift detectors) have improved signal-to-noise ratio and the instrumental detection limits. The current paper presents a method to analyse multiple trace elements in sea water samples using EDXRF technique. The optimized methodology was tested for analysis of sea water samples collected from the Thane creek, Mumbai, India. The results were compared and validated with ICP-AES analysis.

2. Methods

2.1. Standards preparation

The calibration curve method was used for the determination of trace elements in sea water samples. The standard samples required for obtaining calibration curves were prepared using synthetic sea water. The advantage of preparing synthetic sea water is reproducible solution of known composition. Synthetic seawater was prepared using a standard recipe (ASTM, 2013) and had an ionic strength of 0.72 mol kg^{-1} H_2O and salinity of 3.5%. A single batch of synthetic seawater was prepared by adding seawater constituent salts (NaCl, KCl, Na_2SO4, $CaCl_2$, $MgCl_2$) by weight to 16 MΩ Milli-Q water (TKA Pacific). All reagents and solvents used were of analytical quality grade. The pH of solutions was adjusted at pH 6 by using 1 N nitric acidor sodium hydroxide. The multi-element standard having concentration of 10 ppm (Thermo-Fisher Scientific, ICP Standard solution) was added to the synthetic water. Altogether, 5 standard aliquots were prepared for calibration having concentration of 10, 20, 50, 100 and 200 ppb respectively. The trace metals in seawater samples were pre-concentrated for simultaneous quantitative determination using solvent extraction procedure. The synthetic seawater samples (400 mL) were placed in a separating funnel for chemical processing. 4 mL of 1% APDC and 20 mL of MIBK were added into it. MIBK is preferred because of its efficiency to extract wide range dithiocarbamate-metal chelates (Danielsson et al., 1982; Bone and Hibbert, 1979). The samples were shaken for 30 min and allowed to stand for 20 min for phase separation. The lower seawater phase was drained and the organic phase with metal complexes was left for drying on mylar substrate. In particular, APDC acts as a complexing agent which forms complexes with trace metals in sea water and transfer it to MIBK solution in extraction process. The evaporation of volatile organic solvents results in thin film of elemental deposition on mylar substrate. These films were used for counting in the EDXRF instrument.

Table 1
The EDXRF parameters used for counting the fluorescent X-Ray pulses from the pre-concentrated thin film samples[a].

Elements	Secondary target/Filter	Current (μA)	Voltage (kV)	Preset Time (Second)	Energy range (keV)
Ga, Se	Zr Target	4800	50	600	0–40
V, Cr, Fe, Co, Zn, Sc	Ge Target	4000	40	400	0–40
As, Cd, Pb	W Filter	900	49	800	0–40

[a] All measurements were made in air atmosphere.

2.2. Instrumentation

All measurements were carried out using the Xenemetrix EX-6600 EDXRF spectrometer. The instrument consists of an X-ray tube with a Rh anode as the source of X-rays with 60 kV and 6.6 mA power supply, a LN2 cooled Si(Li) detector with a resolution of 131 eV at Mn Kα (5.9 keV) X-ray and a 8 sample turret that enables mounting and analysing 8 samples at a time. The inbuilt nEXT software was used for quantitative analysis of samples. To optimize the EDXRF sensitivities for the wide range of elements, three different combinations of EDXRF parameters (including voltage and current) shown in Table 1 were utilized. The secondary targets of particular line energies and filter were used to for selective excitation of sample elements (Singh et al., 2011; Tiwari et al., 2013). Secondary targets emit their own characteristic radiation without a white background (except the scattered part of the primary beam). Accordingly, the zirconium target was used for quantification of Ga and Se; and germanium target was used for the quantification of V, Cr, Fe, Co, Zn and Sc. The choice of filter should be such that its absorption edges are at lower wavelengths than the wavelength domain to be transmitted (Van Grieken and Markowicz, 2001). The W filter was used for detection of As, Cd and Pb. Pb and As are two elements that share one of the main lines of dispersion in the EDXRF spectra (Pb Lα and As Kα are at the same energy). Pb concentration is calculated directly from its intensity of Lβ energy. As concentration was calculated using intensity ratio method (Tiwari et al., 2014). The instrument response was calibrated for the conditions given in the Table 1 using the standard samples of varying concentration prepared in the laboratory.

3. Results

As discussed earlier, the pre-concentrated thin film samples were analysed using different secondary targets and filters to improve the signal to noise ratio. The advantage of thin film samples is that it is not necessary to apply matrix correction in the XRF analysis. The typical EDXRF spectrum obtained for the standard sample using germanium target is shown in the Fig. 1. The intensity counts obtained for varying concentration of standard samples were analysed to generate the linear regression plots. The average counts obtained for different elements corresponding to their concentration is displayed in the Fig. 2. The EDXRF response function was found to be linear for 11 elements within the concentration range considered in this study (0 – 200 ppb). The R^2 values ranged from 0.97 to 0.99 as stated in the Table 2. The reproducibility or precision of the method was tested by processing and analysing multiple standard samples having concentration of 10, 20, 50, 100 and 200 ppb each. The method was found to be reproducible with maximum variation of 8%. The recovery percentages of elements were calculated for the method by analysing the spiked standards. The multi element standard of know concentration was spiked in the standard samples and analysed. The recovery of the elements ranged from 75% to 95%. Thus the optimized method was found to be limited in terms of accuracy. This has mainly to do with the sample loss in the