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PREPARATION OF THIN FILM STANDARDS FOR TRACE ELEMENT STUDIES IN WATER

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ABSTRACT

Three methods namely Precipitation Separation technique, vacuum vapour deposition and solution deposite methods were chosen for the preparation of thin film standards. Recovery of the material, reproducibility of the procedure, uniformity of the standards and XRF spectrometer sensitivity tests for Fe, Zn and Pb were conducted. Precipitation separation technique was seen to be a promising technique for such a work.

INTRODUCTION

A lot can be learned about our environment through advanced techniques such as X-ray fluorescence (XRF) and Patrticle induced X-Ray Emission (PIXE). These techniques are non destructive, which permits samples to be retained for further analysis. Through sample preparation efforts involved in many cases are simple, but when these techniques are employed for trace element analysis of water samples, the problem of sample and standard preparation becomes complicated. To obtain low matrix effects and high sensitivity water must be removed and microgram quantities of the solute in the from of thin film deposited on a support material (filter paper) must be reduced to dryness, without significant alterations in the concentration of the trace elements present. Milipore filter paper, with regards to trace impurities and pore size was considered to be very suitable for such work.

To perform quantitative measurements of trace element impurities in water samples, the characteristic x-ray intensities corresponding to various elements present has to be converted to mass concentration ($\mu g/cm^2$). Therefore it becomes necessary to prepare a set of standards, whose chemical composition is known to a high degree of accuracy. The parameters that effects x-ray intensity-concentration relationship are:

i) Distribution of material through the paper
ii) Absorption or enhancement of spectral lines by other elements present
iii) Reproducibility of the procedure
iv) Sensitivity of response in counts per second per microgram.

For thin samples, matrix absorption enehancement effect is negligible. From the data available [1,2] samples can be regarded as thin layer according to the thin film criterion $m\mu < 0.1$. Where μ (cm^2/g) is the total mass attenuation-coefficient for the primary and excited radiations and $m(g/cm^2)$ is the mass per unit area of the sample. Samples of mass 200-600 $\mu g/cm^2$ depending on the element can be taken as thin samples [3].

Various methods commonly employed for thin film preparation are

i) Boiling and freez drying [4],
(ii) Ion exchange resin method [5,6,7],
(iii) Precipitation Separation Technique [8,9,10], (iv) Solution Deposit Method [11,12,13,14], (v) Vacuum Vapour Deposition Method [15,16,3].

PREPARATION OF STANDARDS

The object of this work was to make a comparative study of different methods available for standard preparation for the analysis of water samples to be used in combination with Energy Dispersive x-ray Fluorescence method. Attempts to produce samples or standards by boiling or freez drying process were discarded as in these processes, large amounts of solutions are lost from the surface. Moreover there is a risk of contamination from the atmospheric dust particles, if an open system is used. Ion exchange resin method was also not considered, because of the complexity of chemistry involved due to the selection of specific ion exchange resin for different groups of element [17]. A blank standard was included in each x-ray intensity vs concentration graph.

Precipitation Separation Technique

This technique needs a suitable element to be added to the liquid sample of known elemental concentration to act as a coprecipitant. The solution is adjusted to the proper PH value and the elements [one or more] are precipitated quantitatively with a suitable organic or inorganic precipitant. The solution is then filtered through a filter paper. The trace elements in this way are deposited uniformly over a relatively large area.

Elements that can be precipitated for a PH value of 4 using Sodium di-ethyle di-thiocarbamate (NaDDTC) in the presence of copper as a co-precipitant are shown in fig.(1) [9]. Milipore filter of pore size 0.45 micron was used to collect the precipitate. This pore size is considered sufficient for a complete recover of even a fine precipitate [18]. Metal solutions of 1 PPM and 10 PPM concentrations for the metals Fe, Zn, Pb were prepared in distilled water. Volumes of the solution were chosen to obtain different amounts of material as shown in the Table (1). To each portion 10 ml of copper solution (1000 PPM) was added, then 10 ml of accetate buffer solution and a few drops of mixed indicator were added. Thereafter HCl was added drop by drop till the colour of the mixture changes from yellow to violet (PH4). In the end 5 ml of freshly prepared 2 % NaDDTC was mixed and the solution was allowed to stand for 5 minutes to ensure complete precipitation. Finally the solution was filtered through the filter paper. The deposition of precipitate was confined to an area of 9.73 cm^2. It was then dried in a desicator. Blank standard was also prepared in the same way except that it does not contain standard metal solution.

Solution Deposit Method

In this method, standard solutions of the reagent grade metals were prepared using distilled deionized water. Each standard solution was deposited with a precision micropipette in 50 1 amounts in the center of the paper. The solutions were then allowed to dry in air.

Vaccum Vapuor Deposition Method

In this method, a blank filter paper was precisely weighed and then placed on a mask having a hole of 10 mm diameter in size. A distance of

4 cm was maintained between the mask and the boat containing pure element of interest, the voltage and current values were adjusted according to the nature of the metal. After deposition, the paper was reweighed and the total mass of the element deposited was determined. As the area of the circular deposit was known, the mass/cm^2 for each standard was calculated. A set of standards with varying amounts of deposit was prepared for each element of interest.

RESULTS AND DISCUSSION

Precision of these methods for standard preparation was determined by the magnitude of the recovery of elements under study, reproducibility of the procedure, uniformity of the material distribution through the filter paper and sensitivity of response in counts per second per microgram. These tests were under taken for the precipitation separation technique. Recovery checks were made by running Iron and lead standards under optimum operating conditions Table (4). X-ray intensity vs concentration relationships were obtained and found to be linear. As a cross check the standards supplied by micromatter were used as unknown samples and their concentrations were determined using the x-ray intensity vs concentration relationship. The results are shown in the table (2).

In order to check the reproducibility of this technique, three independently prepared set of samples were run for x-ray intensity measurements. For the intensity measurements, the samples were irridiated by x-rays from the x-ray tube (EG&G Ortec 3150).Filters available were copper (Cu) and molybdenum (Mo). On irridiating, atoms of the samples with primary x-rays of sufficient energy, their characteristic x-rays were emitted. These were detected by a Si(Li) detector. For characteristic x-ray intensity measurements of Iron and Zinc K_α lines and for the heavier element lead L_α line, were used. The optimum operating conditions referred earlier were used for this test also. Each measurement lasted for 400 seconds.This time was chosen to ensure good counting statistics. The total x-ray counts for 400 seconds counting time for the three samples are given in the Table (3).

For uniformity checks, x-ray intensity scan across the arbitrarily chosen diameters AB and CD fig (2a) was made. Results of a typical standard for (Pb) are shown in fig. (2b, 2c). For each observation, the standard was shifted along the diameter by 3 mm. The error bars in the figure represents the counting statistics and uncertainity in the target orientation.

The standards prepared by precipitation separation technique shows reasonably good magnitude of recovery for the material.Reproducibility and uniformity is also of reasonably high standard.

The standards prepared by solution deposite method and vacuum vapour deposition were also checked for reproducibility and uniformity. In case of the samples prepared by solution deposit method, the filter paper was found not to wet uniformly. As in the XRF method used, the primary x-ray beam was 3 mm in diameter. Therefore the results obtained for aereal uniformity were not as good as for the standards prepared by the precipitation separation technique. In case of vacuum vapour deposition method, the reproducibility and aeral uniformity were as good as those obtained in the case of precipitation separation technique.

Sensitivities of the XRF spectrometer for the elements Fe, Zn and Pb were measured using the sets of standards prepared by the three methods chosen for this work. Net peak intensity above the background vs concentration relationship (calibration curve) for each of the methods used was obtained. One such set of curves for the element Fe is shown in fig.(3). From these the sensitivity values for the elements were calculated and are given in table (4).

Results obtained by precipitation separation technique and vacuum vapour deposition methods are comparable, where as, there is a marked improvement in their values, when compared to those obtained by solution deposition method.

It is obvious from the results, that for the analysis of water samples, the precipitation separation technique for the preparation of standards is very promising. The standards are uniform and highly reproducible. Moreover by the use of a wide band precipitant a number of elements can be precipitated quantitatively at the same time. Another advantage, which makes this method more suitable for the analysis of water samples is that, preconcentration of trace elements in the unknown samples can be achieved prior to their determination by following exactly the same procedure as used for standards preparation.

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Table - 1 : Amounts of material chosen for standard preperation

Element	Amount of material in μgm				
Fe	5,	10,	20,	50,	90,
Zn	5,	10,	20,	30,	40,
Pb	5,	10,	20,	50,	100,

Table - 2 : Recovery Checks

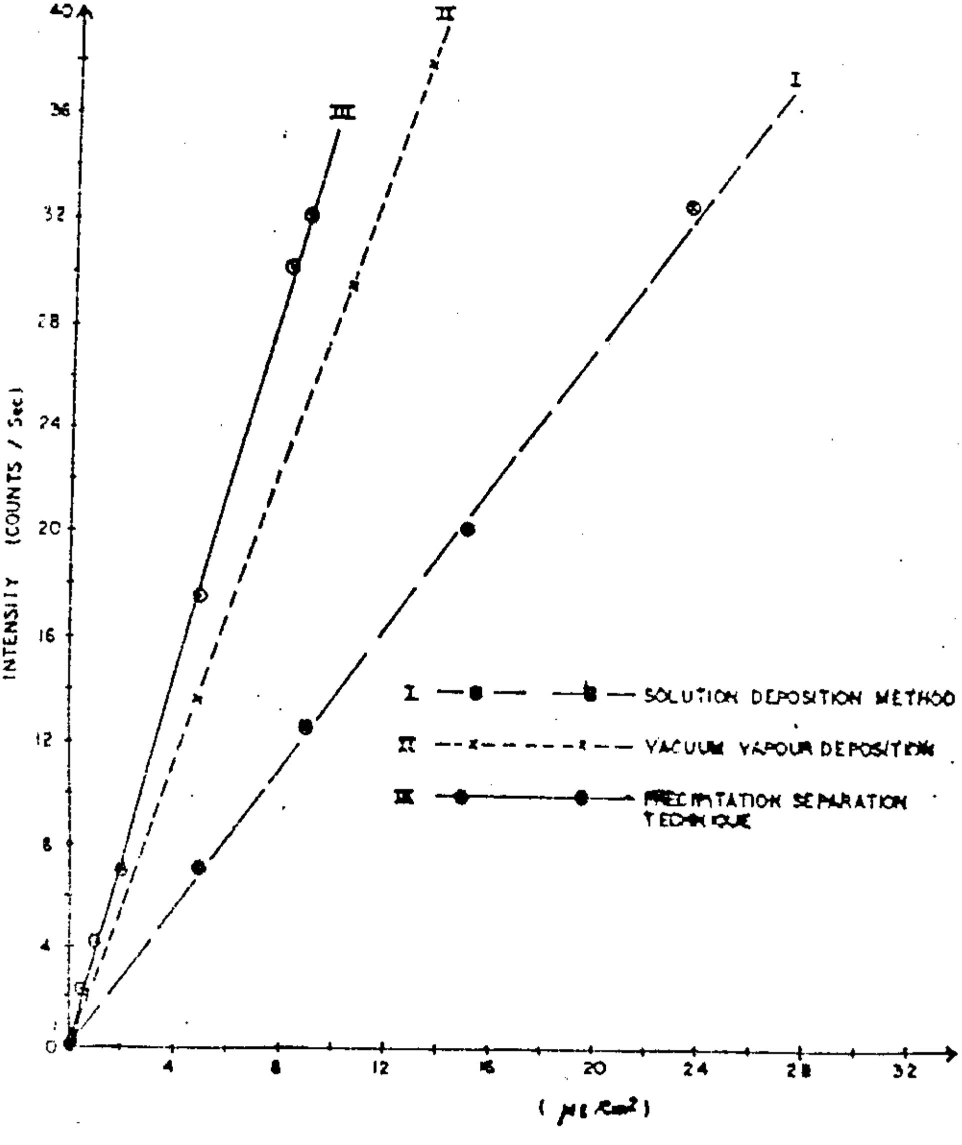
Element	Concentration in μg/cm2		Deviation
	Input	Measured	
Fe	54.00	54.03	0.03
	54.00	54.039	0.039
Pb	126.00	126.128	0.128
	126.00	126.107	0.107

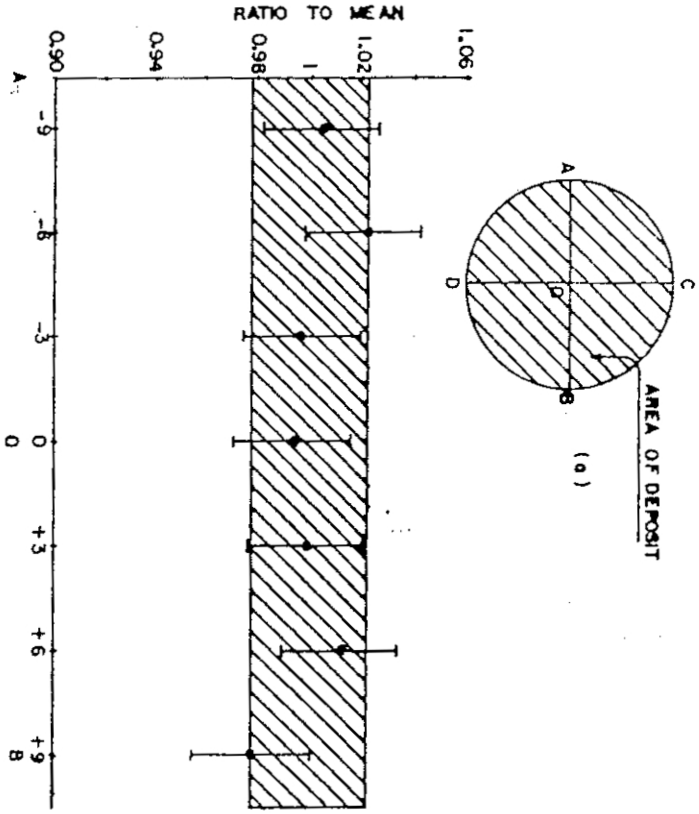
Table - 3 : Reproducibility for 400 Second Count time.

Element	Total Counts for the Sample No.1	 No.2	 No.3	Standard Deviation
Fe	5968	6113	5819	2 %
Zn	9860	9713	8870	5 %
Pb	8851	8011	8939	6 %

Table - 4 : XRF Spectrometer Element Sensitivities

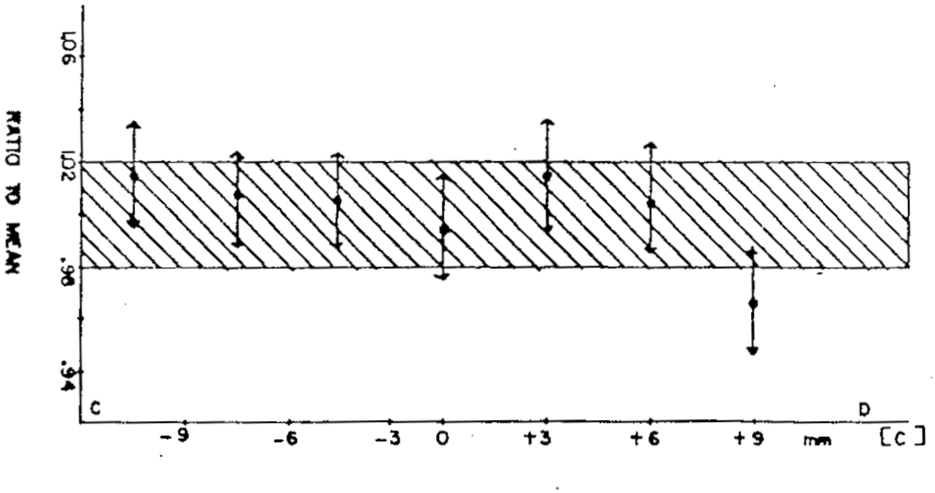
Element	Spectral Line	Instrumental Condiditons KV	 μA	 Filter	 X-Ray Path	Sensitivity (Counts 400 sec/μg/cm) Solution Depos.	 Vacuum Depos.	 Precipitat. Deposition
Fe	K_α	45	100	Mo	Vacuum	542	1200	1299
Zn	K_α	40	180	Mo	Vacuum	180	2000	2897
Pb	L_α	40	180	Mo	Vacuum	140	1050	1000


40
36
32
28
24
20
16
12
8
4
0
INTENSITY (COUNTS / Sec)
III
II
I
I —●— —●— SOLUTION DEPOSITION METHOD
II --x-- ----x-- VACUUM VAPOUR DEPOSITION
III —●——●— PRECIPITATION SEPARATION TECHNIQUE
4
8
12
16
20
24
28
32
(μg /cm²)

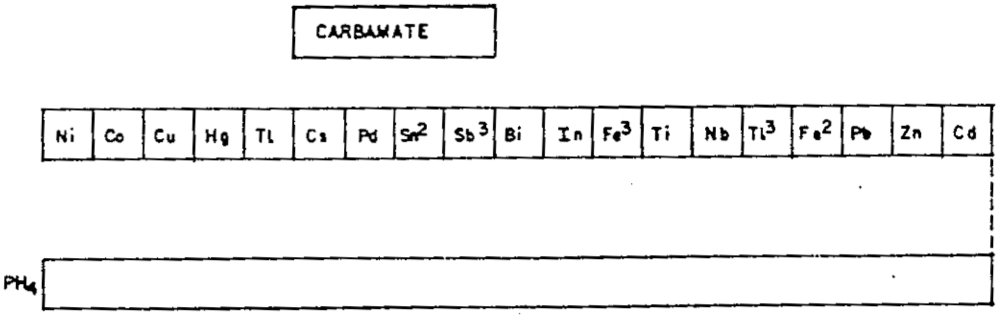


(a)

(b) POSITION ALONG THE DIAMETER (AB) (mm)



(C) POSITION ALONG THE DIAMETER CD (mm)


CARBAMATE
Ni
Co
Cu
Hg
Tl
Cs
Pd
Sn2
Sb3
Bi
In
Fe3
Ti
Nb
Tl3
Fe2
Pb
Zn
Cd
PH4