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DETERMINATION OF TRACE ELEMENTS IN COASTAL WATERS BY X-RAY FLUORESCENCE TECHNIQUE

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ABSTRACT

Energy dispersive X-ray fluorescence technique was employed for the determination of trace elements in coastal waters of Saudi Arabia. Samples were collected from Arabian Gulf. Sensitivity and detection limits of the spectrometer for different elements and their concentrations were determined. The elements studied were iron, nickle, zinc and copper.

INTRODUCTION

In recent years X-ray fluorescence analysis has emerged as a powerful technique for the elemental analysis. Traditionally X-ray tubes have been employed to excite the elements in the sample and their characteristic X-rays are dispersed according to their energy by a semi-conductor detector. The energy dispersive spectrum is then analysed by the multichannel analyser. The non destructiveness of this method and its fairly uniform detectability across the periodic Table are its main attractions [1,2,3].

If samples to be analysed are thin, the tailing background, which arise due to scattering of radiation from the sample is low. Moreover, matrix absorption enhancement effect is easily estimated [4,5]. From the data available [6,7] samples can be regarded as thin layers according to the thin film criterion $m\mu < 0.1$, where 'm' is the mass per unit area of the sample and is the total mass attenuation co-efficient for the primary and excited radiations. Samples of mass 200-600 microgram per cm2 depending on the element can be regarded as thin

EXPERIMENTAL SET UP, SAMPLE PREPARATION AND TESTING

The specimen under study was irradiated by a primary beam from the x-ray tube (model EG&G ORTEC 3150). A Si(li) detector, absorbs the energy of each X-ray photon that passes through its very thin window (0.008 mm thick) into its sensitive volume. The measured detector resolution was 157 eV FWHM at 5.9 KeV from Mn K_α at a shaping time constant of 10 μ sec.

Energy spectrum was initially examined visually with the help of a multichannel analyser, for the data that was desired and information were recorded or transferred to online computer for further reduction.

For quantitative analysis, the observed X-ray line intensity has to be converted to elemental mass concentration. The observed X-ray intensity, will however be reduced or increased (absorption enhancement effect) due to the presence of other elements. The concentration of the ith element is given by the equation.

$$C_i = A' + B'[\exp(-M_{ij}C_j)] \qquad (3)$$

where, M_{ij} is the interaction co-efficient for the element 'j' on element 'i' and 'C_j' is the concentration of the jth element.

The interaction co-efficient was first determined by a non-linear multiple least square fit of the concentration Vs intensity relation for the standards. Later on, the elemental concentration in unknown samples was calculated with an iterative process using eqn.(3).

Water samples were collected from different places along the Gulf coast of the Kingdom of Saudi Arabia. These were from (1) Ras Tanura Port, (2) 1 1/2 km from Ras Tanura, (3) 2 1/2 km of Dammam Port, (4) Dammam Port, (5) Blow down area (waste disposal from desalination plant), (6) 120 meters from the blow down area. These locations are marked in the Fig.(1).

Thin calibration standards and water samples for the elememtal study were prepared by precipitation separation technique [9,10]. The elements selected were Fe, Ni, Zn and Cu.

For calibration standards, metal solution of known concentration for the element Fe, Ni, Zn and Cu were adjusted to PH4 and to each portion, 10 ml of the Copper solution (1000 pm) was added as a co-precipitant. The quantitative precipitation was then carried out by adding 2% freshly prepared solution of sodium di-ethyle di-thio carbamate (NaDDTC). The solution was allowed to stand for 5 minutes and then filtered slowly through a Millipor filter of pore size 0.45 microns. This resulted in a thin uniform circular deposit of precipitate on the filter paper. From the area of the deposit, the amount of each element deposited per unit area was calculated. Blank standard for each element was also prepared in the same way expect that the standard metal solution was not added. In case of unknown water samples, water was removed and a thin film of microgram quantities of trace elements was obtained by following the above mentioned procedure.

Uniformity and reliability of calibration standards thus prepared was examined experimentally. Reliability checks were made by analysing unknown samples, using the thin calibration standards prepared by the precipitation separation technique and those obtained commercially, prepared by evaporation technique [11]. Results of the elemental concentration for one of the elements, (Fe) for the two types of standards is shown in the Table (1). The results show that the reliability is with-in fairly acceptable limits.

COMPUTATION OF RESULTS AND DISCUSSION

For quantitative analysis, the samples were analysed under optimum operating conditions. Under these conditions signal/noise ratio was maximum. For such conditions, X-ray spectrum of one of the samples is shown in Fig.(2). Various other factors affecting the accuracy of the results, such as (a) instrumental drifts, (b) statistical fluctuations in the count rate, (c) operational errors, (d) matrix absorption enhancement effects and (e) spectral interference were carefully considered. The effects a,b and c were studied by repeating the intensity measurements for a few prominent lines in the spectrum. The stability of measurements was observed to be + 0.512%. For matrix absorption enhancement effect, the most likely case was the enhancement effect on Fe(kα) in the presence of Ni. Both Ni(kα) and Ni(kβ) lines lies on the short wavelength side of Fek absorption edge. This was studied by preparing samples with varying amounts of iron and nickel. The iron concentrations varied from 0.25 μg/cm^2 to 15 μg/cm^2 where as nickel varied from 0.05 μg/cm^2 to 3.08 μg/cm^2. These values were chosen keeping in mind the expected concentrations of these elements in the samples under study. The excellent linearity suggests that within the concentration range chosen, the absorption enhancement effect was negligible (see Figs.3&4).

The measured sensitivity of the X-ray spectrometer and detection limits obtained for 400 seconds counting time interval on elements under study using thin film calibration standards are list in Table II

The concentration values of various elements present in the samples are given in the Table (III) and are also shown in the bar graph Fig.(5). Concentration values of Fe varies from 2.2 μ g/litre for sample No.3 to 34.85 μg/litre for sample No.5. Ni was minimum for sample No.4 and maximum for sample No.5. Zn and Cu concentration were minimum for sample No.2 and maximum for the specimen No.5. It is clear that the specimen No.5, which is taken from blow down area in Al-Khobar has the maximum amount of trace impurities. Present results are also comparable with similar studies for the waters from Indian Ocean and Arabian Sea, carried out by other workers Table (IV).

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FIGURE CAPTIONS

Fig. - 1 : The sampe locations.

Fig. - 2 : X-ray spectrum of a water sample.

Fig. - 3 : X-ray intensities of Fe (k_α) Vs Fe concentration in the presence of Ni.

Fig. - 4 : X-ray intensities of Ni (k_α) Vs Ni concentration in the presence of Fe.

Fig. - 5 : Bar graph for Fe, Ni, Zn and Cu.

Table - I : Reliability checks of calibration standars

Sample No	Iron concentration as determined by	
	Precipitation Separation technique μg/litre	Evaporation technique μg/litre
1	24.25	24.96
2	6.81	7.03
3	2.22	2.36
4	6.51	6.8
5	34.85	35.6
6	11.34	12.05

Table - II : Measured sensitivies and detection limits of the X-ray spectrometer for different elements

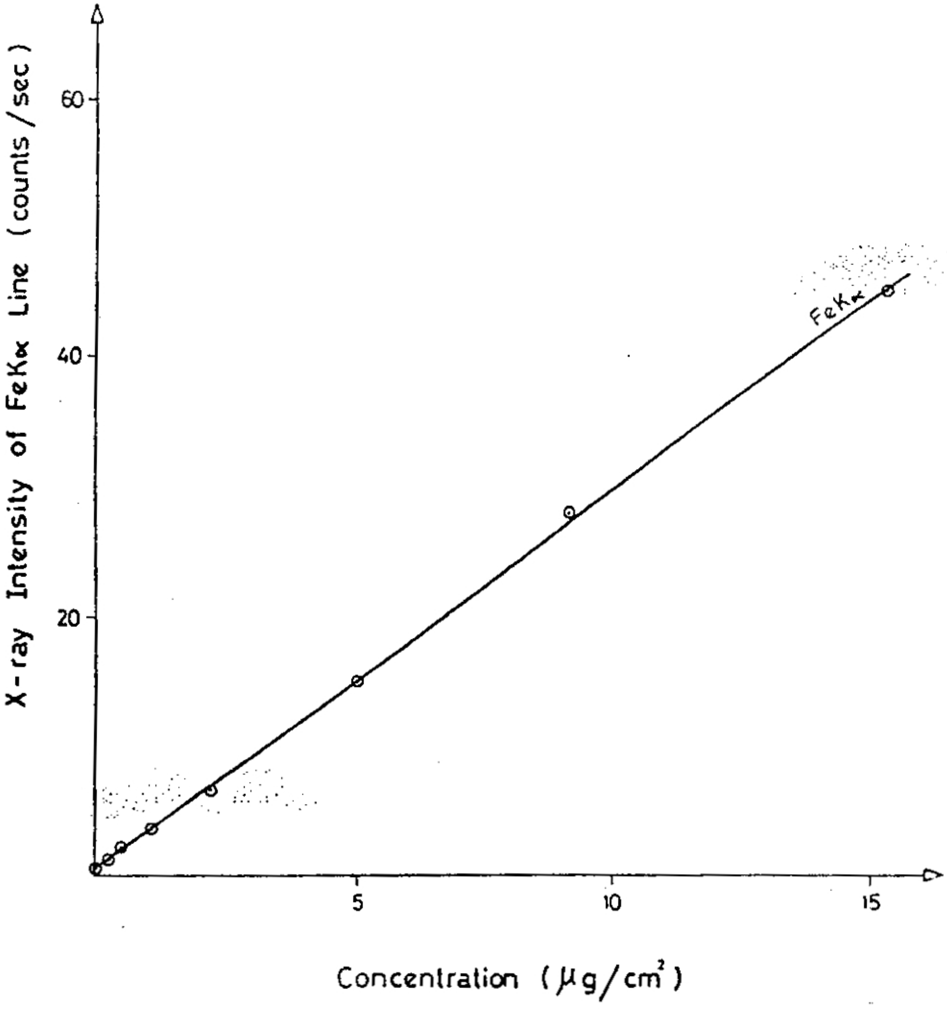
Element	Sensitivity counts/400 sec	Detection limit ng/cm^2
Fe	1200	28
Ni	1440	23
Cu	1680	10
Zn	2860	7

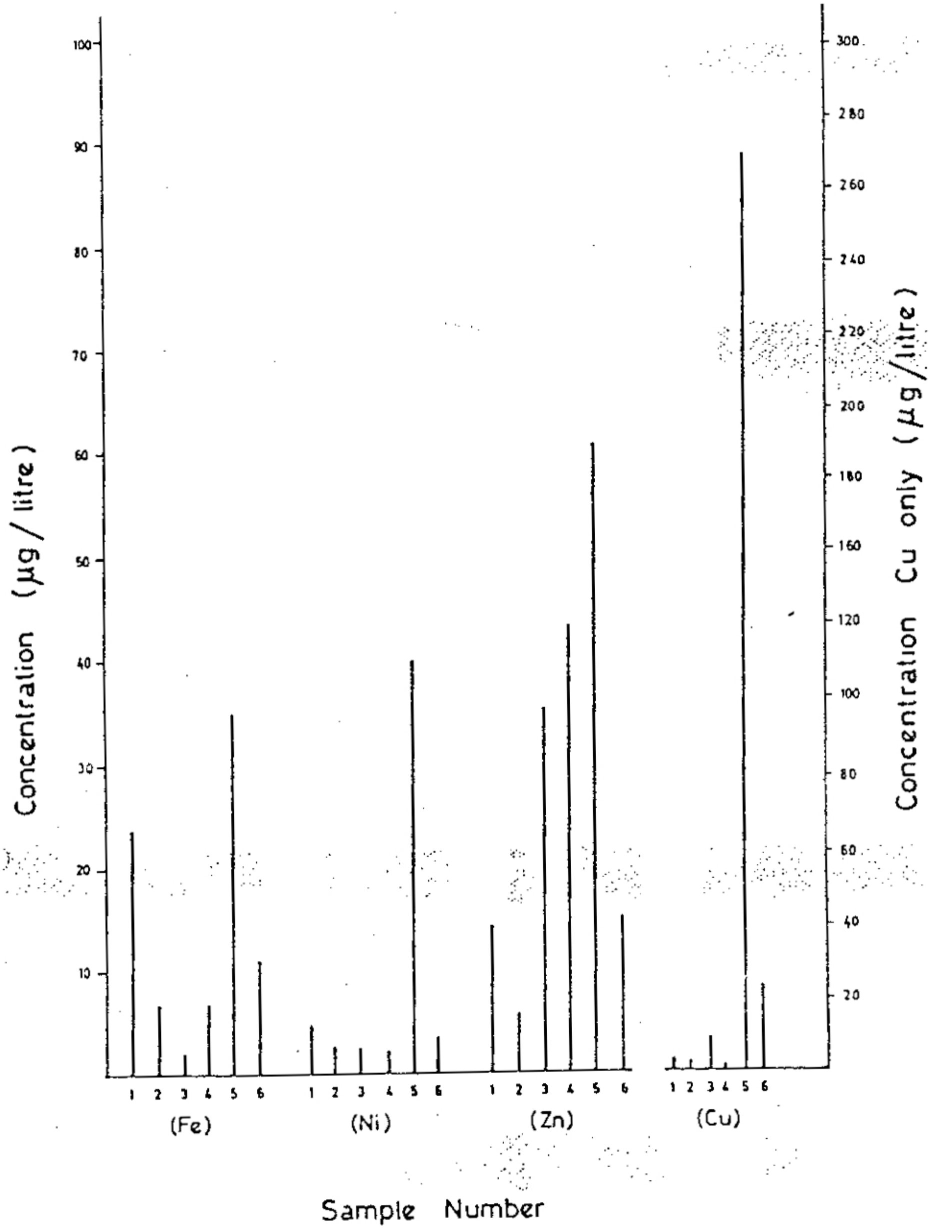
Table - III : Elemental concentrations in µg/litre of sea water

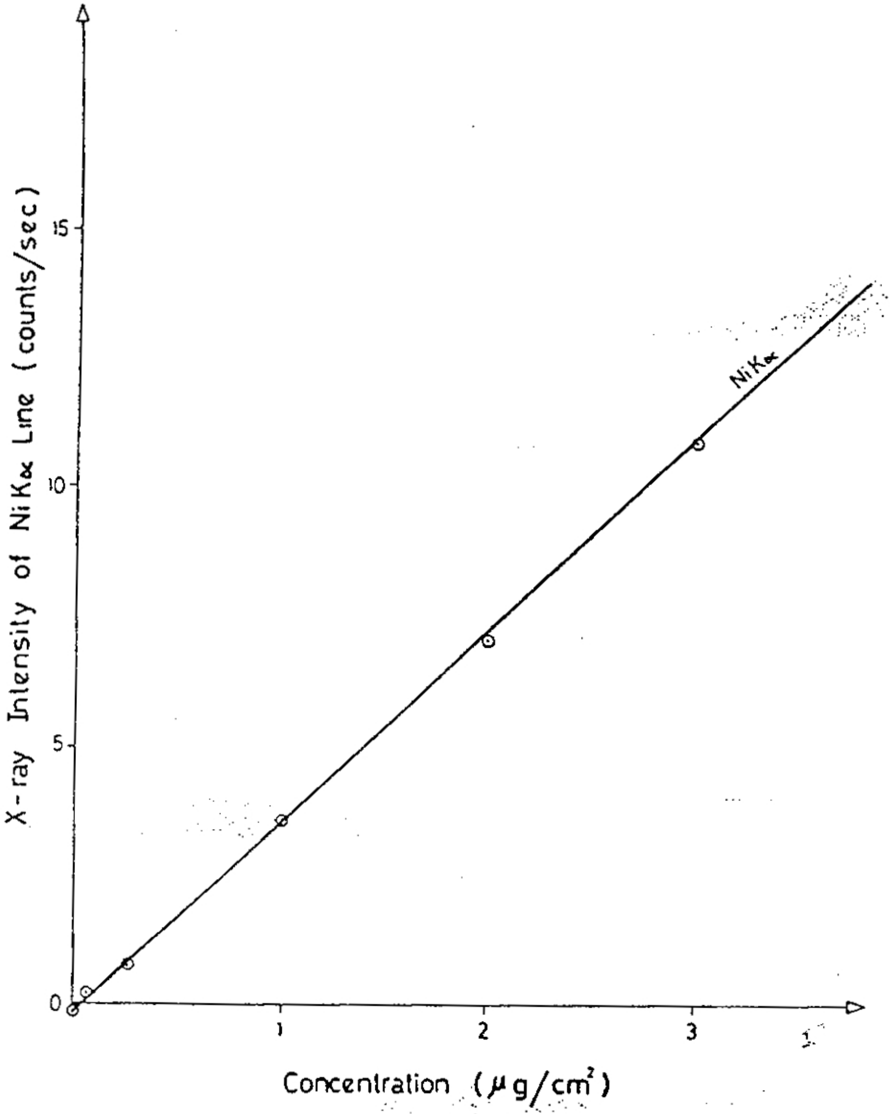
Sample Element	No.1	No.2	No.3	No.4	No.5	No.6
Fe	24.2	6.8	2.2	6.5	34.8	11.34
Ni	4.36	3.16	2.92	2.2	39.69	3.66
Cu	5.6	3.8	9.3	3.5	268.6	24.7
Zn	14.31	5.2	35.6	42.8	60.5	13.99

Tablo - IV : Comparison of present results with other similar studies

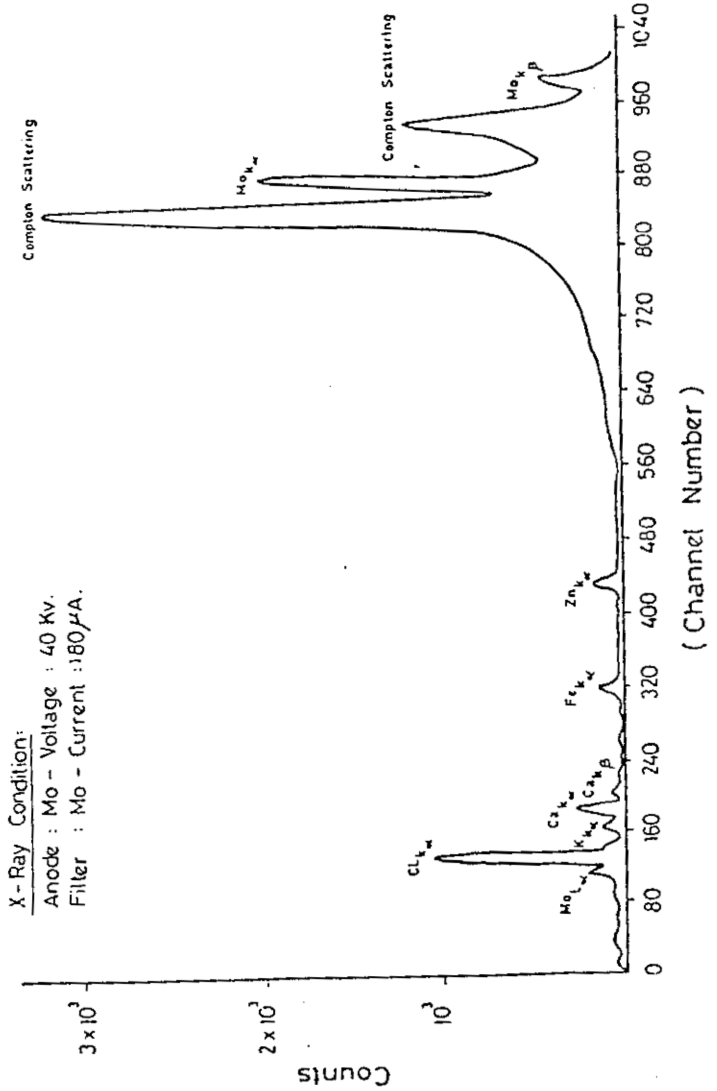
	Concentration in µg/litre			
References	Fe	Ni	Cu	Zn
Graham topping (1969) [12] Indian Ocean and Arabian Sea	.1-61.8	-	.3-3.2	3.9-48.4
Fonselias S.H (1970) [13] The Mediterranean, the Red Sea and Arabian Sea	-	-	zero-2.9	1.0-26.7
Present work (Arabian Gulf)	2.2-34.8	2.2-39.6	3.5-268.6	5.1-60.5


X-ray Intensity of FeKα Line (counts/sec)
60
40
20
FeKα
5
10
15
Concentration (μg/cm²)


Concentration (μg / litre)
100
90
80
70
60
50
40
30
20
10
Concentration Cu only (μg / litre)
300
280
260
240
220
200
180
160
120
100
80
60
40
20
1 2 3 4 5 6
(Fe)
1 2 3 4 5 6
(Ni)
1 2 3 4 5 6
(Zn)
1 2 3 4 5 6
(Cu)
Sample Number


X - ray Intensity of Ni Kα Line (counts/sec)
0
5
10
15
Ni Kα
1
2
3
Concentration (μg/cm²)


Arabian Gulf
1
2
3
4
5
6
Dammam
Riyadh
Jeddah
Red Sea


X - Ray Condition:
Anode : Mo - Voltage : 40 Kv.
Filter : Mo - Current : 180 μA.
Counts
3 x 10³
2 x 10³
10³
(Channel Number)
0
80
160
240
320
400
480
560
640
720
800
880
960
1040
Mo Lα
Cl Kα
K Kα
Ca Kα
Ca Kβ
Fe Kα
Zn Kα
Compton Scattering
Mo Kα
Compton Scattering
Mo Kβ