2

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CONCENTRATION OF TRACE INORGANIC IONS FROM AQUEOUS
SOLUTIONS FOR ANALYSIS BY X-RAY FLUORESCENCE SPECTROMETRY

- A Status Report -

Carol H. Fuchs* and Richard W. Ryon

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MASTER

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2/8

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CONCENTRATION OF TRACE INORGANIC IONS FROM AQUEOUS
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INTRODUCTION

The contamination of surface and ground waters by heavy metals and other inorganics by such sources as strip mining operations, industrial wastes, and urban effluent is of increasing concern. Water is increasingly a recycled commodity. In each pass through the consumption and disposal cycle, the inorganic (as well as organic) impurities increase in concentration. It is estimated that by the late 1970's that the "environmental stress index" for heavy metals will be greater than that for any other pollutant.

Another developing interest is the correlation between metal ions and human health. Both nutritionists and medical researchers need to develop data bases for metal concentrations in foods and biological fluids.

Energy dispersive x-ray fluorescence has the promise of providing the required analyses for all such applications because it has relatively high sensitivity, and because it is a reasonably simple multi-element method. However, many of the potential applications require analyses in the nanogram/milliliter range. In order to make precise measurements at these levels, a pre-analysis concentration step is necessary.

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There are many possible methods of concentrating the inorganic impurities from water. These include:

- 1) Evaporation
- 2) Precipitation
- 3) Electrodeposition
- 4) Ion exchange beads
- 5) Ion exchange impregnated filter papers
- 6) Membrane "filtration"

This paper considers all but items 2 and 3 in varying degrees of detail. It is intended that this be a progress report with further work to follow as time allows.

Ion Exchange Loaded Papers

Work done by Campbell et al.¹ showed that ion-exchange resin loaded filter paper to be a fast and effective method of concentrating inorganic ions. However, the capacity of the papers is relatively low (.02 meg/cm² for Reeve-Angel SA-2 paper). Since our main concern was the analysis of natural waters, the potentially high Ca and Mg concentrations could saturate the papers. We did a series of experiments with Gelman SA-6404 paper which demonstrates this problem. Water containing 12 ppm Cu⁺⁺ and between 0-500 ppm Ca⁺⁺ was passed through the paper (which was in the sodium form) seven times, dried, and the Cu K α fluorescence intensity measured. The results are shown in Figure 1. Clearly, there is a serious inter-element competition which precludes the use of these filters if one ion in the solution exceeds a few μ g/ml.

Evaporation

A previous report²⁾ indicates that as much as a 100-fold improvement in detection limits can be obtained by transferring the metals to be measured from a bulk sample to thin Mylar film. One need only evaporate about 5 ml of solution onto a 5 cm² Mylar film (mounted on a standard "Spex" liquid cell) to obtain detectabilities in the nanogram range.

Experiments were done in the above manner using a vacuum dessicator. If too high a vacuum is used, the solutions boil which causes loss of sample by splattering. When "house" vacuum is used, the water evaporates in 24-48 hours over CaCl₂. When a small amount of a non-ionic detergent is added to the solution, a uniform-appearing deposit is left behind.

Because of the time required to evaporate the samples, perhaps better methods of sample concentration can be found. However, evaporation has three major strong points:

- 1) Very little labor is involved.
- 2) It is universal, i.e., nothing is lost due to chemical or physical specificity.
- 3) The deposit is left on a very thin film (2.5μ), which scatters very little radiation into the detector. Improved counter efficiency and signal-to-noise ratio is thereby obtained.

Membrane Collection

Cellulose acetate membranes such as those used to commercially demineralize water might be used to collect inorganic ions for analysis. This method of impurity concentration has similar advantages as evaporation, namely:

- 1) Unattended operation
- 2) The collection is nearly universal, with only small differences in retention among ions expected.

- 3) The deposit is left on a fairly thin film ($\sim 80\mu$ for commercial membranes).

Water elimination should be faster than by evaporation. One manufacturer states that fluxes of about $1 \text{ ml/cm}^2\text{-hr}$ are achieved. We, therefore, have a time-scale intermediate between resin-loaded papers and evaporation.

There are two methods of forcing water through membranes. The common method used to overcome the osmotic pressure caused by the dissolved impurities is to use pressure (400-1000 psi), either with a piston or high pressure gas. Instead, we chose to take advantage of the osmotic pressure differential created by a solution of an impermeable substance. This allows the use of a very simple apparatus consisting of a cylinder which has the membrane sealed at the bottom with an "O"-ring. The membrane end of the cylinder is immersed in a beaker containing a concentrated sucrose solution. The osmotic pressure differential (which can approach 3000 psi^3) completely dehydrates a 10 cm high solution in 6-8 hours.

Early experiments with standard solutions were very encouraging, giving good sensitivities and high signal-to-noise ratios. However, we encountered severe problems of irreproducibility. Ions were found in the sucrose solution. It was surmised that the problems might be related to membrane inhomogeneity and/or holes in the membranes.

It was felt that we needed to know a great deal more about membrane technology. We have now had discussions with Ronald Fox and James Beckman at the ROGA Division of Universal Oil Products in San Diego. These men were very generous with their time and made several useful suggestions. Among them were:

- 1) Probably the most significant suggestion is very simple. A dye such as Rhodamine-B can be used to check for membrane imperfections. Dyes do not stain the active "skin" side of the

membrane, but do stain the support side. Any hole or scratch will allow dye through the active layer to the support side, where a stain forms. In a quick check of three membrane pieces, two had imperfections.

- 2) The high sucrose concentration may be dehydrating the membrane. The flux rate should be measured as a function of sucrose concentration. It is felt that a 10 cm high solution should dehydrate in a couple of hours.
- 3) Cellulose acetate is most stable at $\text{pH} = 4.6$. Membrane stability decreases exponentially with pH on either side of this point. Depending on time of contact, the membrane may be radically changed, leading to the erratic results we have observed. New membranes being developed by UOP are more stable.
- 4) In the space very close to the membrane, ionic concentrations may become quite high. Since rejection of ions by the membrane is a diffusion process, and since the diffusion flux is proportional to concentration, high losses may occur. Erratic results may be caused by variation in stirring of the solution. If the flux rate is linear with time, ionic build-up at the membrane probably is not a problem.

Ion Exchange Resins

Ion exchange resins are good to use in the sense that they require only a small amount of preparation and their capacity is relatively high. The ions can be collected on the resin using a batch method of stirring the resin in the sample. The resin is completely dispersed in the solution allowing intimate contact with the entire solution. The solvent is then filtered off and the resin is dried and is used as is for XRF analysis. The entire sample preparation requires only an hour and it is possible to prepare several samples simultaneously.

The rest of this report describes several tests made using the ion exchange resin and discusses the feasibility of using this method for low level (ppb) metal ion analysis in water samples.

EXPERIMENTAL

The x-ray fluorescence equipment used is a specially designed energy-dispersive system. It consists of a 50 kV - 50 mA generator and a 2500 watt W x-ray tube as the primary source of excitation. The beam is filtered using Sn for high energy ranges (>4.5 keV) and Cu for low energy ranges (<4.5 keV). The amplifier system incorporates pulsed opto-electronic feedback, pulse pile-up rejector, and live-time correction. The spectrum is accumulated by a 2×1024 -channel pulse-height analyzer with a 100 megahertz A-D converter.

Bio-Rad analytical grade cation exchange resin, AG 50 W-X8, was used for all tests. 100-200 mesh was used because it was available, but finer mesh is recommended. The resin is put into the hydrogen form by stirring with an excess of 3 N HCl for 30 minutes and repeating with fresh 3 N HCl. The mixture is then filtered and the resin rinsed free of acid with large amounts of deionized water. The resin can be dried at 100°C for about an hour.

NOTE: Do not use temperatures above 120°C . Time required may vary with the amount of resin, but charring will occur if the resin is left for long periods of time.

Standards were prepared by dissolving weighed amounts of high purity metals, oxides, or salts, and diluting to known volumes. The standards were chosen to cover a range of atomic number from $Z = 20$ (Ca) to $Z = 92$ (U).

Procedure

100 ml of sample is pipetted into beakers and 1 g of dry prepared resin is added. The mixture is stirred with a magnetic stirring bar for

30 minutes, then filtered by suction through a sintered glass crucible. The resin is dried in the crucible for 30 minutes, and then placed into plastic "Spex" cups covered with quarter mil mylar film. The elements collected on the resin are analyzed using XRF. Linear baseline corrections are made by measuring the background on both sides of the peak.

Effect of Stirring Time

Since the collection of ions by the resin is an equilibrium process, it was necessary to make sure that the mixture was stirred long enough to allow the resin either to pick up all of the ions or to come into equilibrium with the solution. Twelve duplicate samples were prepared by diluting 1 ml of 1688 ppm Ni standard to 100 ml. Two of these solutions were stirred for 5 minutes, two for 10 minutes, and similarly for 20, 30, 45, and 60 min. The suggested procedure was completed and the results are given in Table 1 and illustrated in Figure 2. Even though there is about 5% scatter in the data, there appears to be an upward trend to 30 minutes. In any case, a near maximum concentration on the resin is obtained very rapidly, and a 1/2 hour stirring time is quite adequate.

Table 1

Effect of Stirring Time on Concentration of Captions	
Time (min)	Intensity* (cps)

5	67.1 $\pm$ .04
10	68.9 $\pm$ 1.7
20	66.8 $\pm$ 8
30	72.3 $\pm$ 2.8
45	70.4 $\pm$ .07
60	68.7 $\pm$ .47

*The range of values are for duplicate analyses. The 3σ value based on counting statistics is ± 1 .

A stirring time of 30 minutes was used on the remainder of these tests.

Effect of Volume

Since it would be possible to use this method for very low concentrations (ppb range) if the solutions could be concentrated say 1000:1 times, tests were run to check the effect of stirring one gram of resin in various volumes of solution. The solutions were prepared with equal amounts of Ni diluted to a specified volume. 20 ml aliquots of 3.38 ppm Ni were diluted to samples of 50, 100, and 1000 ml. (to give solutions containing 1.3, .68, and .068 ppm Ni). These test solutions were carried through the suggested procedure using 1 g of resin in each. (The 1000 ml solutions were stirred for 1 hr). This had the effect of concentrating the solutions 50:1, 100:1, and 1000:1 respectively. Table 2 shows that the volume has no effect on the ability of the resin to collect the ions. Therefore, by using larger volumes of solutions, smaller concentrations can be analyzed. Most subsequent experiments used volumes of 100 ml, since this volume is easy to work with.

Table 2

Effect of Volume		
67.6 μ grams Ni ⁺⁺		
Volume (ml)	Concentration (ppm)	Counts/sec* NiK α
50	1.352	3.05 + .02
100	0.676	3.19 + .36
1000	0.0676	2.96 + .47

* Ranges of values are for duplicates. The 3σ value from counting statistics is ± 0.3

Recovery

Since recovery of ions from solution is an equilibrium process, it would be possible for equilibrium to occur before all of the ions have been collected onto the resin. In order to check this, three test solutions were prepared using 20,000 μ g Ca, 2790 μ g Fe, 2200 μ g Cu, and 2000 μ g Sr in each.

Three other solutions were prepared with 2790 μg Fe, 2200 μg Cu, and 2000 μg Sr in each (that is, the same as before except Ca was omitted). Each of these solutions was diluted to 100 ml and mixed with 1 g resin. After stirring each mixture for 30 minutes, it was filtered through a sintered glass crucible, preserving the filtrate. This filtrate was again mixed with 1 g resin for 30 minutes and filtered. The process was repeated a third time to produce a total of 3 resin samples for each of the six solutions. The samples were then analyzed by XRF to determine recovery. The number of counts from the first resin was divided by the total number of counts from all resins to determine the percent recovery on the first pass. The results of this test, shown in Table 3, indicate that one stirring of the solution is adequate to recover essentially all of the ions.

Table 3

Sample No.	:	Percent of Ions Collected During First Stirring			
		Percent Recovered During First Stirring			
		Ca	Fe	Cu	Sr
1		>99	96	94	99
2		>99	97	94	98
3		>99	98	94	98
4		-	99	97	>99
5		-	99	99	>99
6		-	>99	98	>99

Inter-element Effects

The results of the previous test were also used to demonstrate the problem of inter-element effects in the x-ray fluorescence analysis. Table 4 indicates the integrated peak heights for the Ca, Fe, and Cu peaks in counts per second. The expected number of counts, taken from a standard solution of each element

in solution by itself, is listed in the first row of the table. The Cu peak height appears to be slightly lower than that expected while Fe and Ca are higher. The rise in the Fe and Ca peaks are due to enhancement effects.

Table 4
Integrated Peak Heights for Inter-Ion Tests*

Sample No.	Ca (cps)	Fe (cps)	Cu (cps)
Expected	10 ± 1.5	89 ± 3	122 ± 6
1	17.3	91.7	108
2	17.2	92.4	110
3	16.4	91.6	111
4	-	104.6	125
5	-	106.1	130
6	-	107.0	125

*Indicated ranges are 3σ values from counting statistics

Since the Cu peak (8.04 keV) is close to the Fe absorption edge (7.11 keV), Cu has an enhancement effect of raising the number of counts in the Fe peak. The iron and copper in turn enhances the Ca fluorescence. Conversely, the Fe and Cu experience absorption, as seen by their increased intensity when Ca is not present. The concentrations in these experiments are higher than would be found in a typical water sample and in normal cases the enhancement and absorption would be much less than indicated here. The error resulting from ignoring inter-element effects is small but very accurate work demands corrections.

Linearity of Response

We checked the linearity of response over a range of 10^4 in concentration. Test solutions were prepared with concentrations varying between 6.76 ug Ni and 67,600 ug Ni. Each solution was treated by the suggested procedure and $\text{NiK}\alpha$ measured. As Figure 3 illustrates, the response is linear from the lowest concentration up to about 50 milligrams of Ni. At the upper end of the range, the 5 meq./g capacity of the resin is being approached. In addition, the Ni is approaching 5% loading on the resin, and some self-absorption is to be expected.

Selectivity Among Competing Cations

No actual tests were made to determine the selectivity among the cations. However, Campbell^{1.)} states, "The affinity of a cation exchange resin for cations of the same valence increases with increase in atomic number of the cations." The Chemist's Companion: A Handbook of Practical Data, Techniques, and References^{4.)} gives the following selectivity orders for cation exchange resins:

TABLE 5

Relative Ion Exchange Resin Affinities for Cations

M^{1+}	: Ag > Tl > Cs > Rb > NH_4 > K > Na > Li
M^{2+}	: Pb > Ba > Sr > Ca > Mg > Be
M^{2+}	: Zn > Cu > Ni > Co > Fe > Ba > Sr > Ca > Mg
M^{3+}	: La > Ce > Pr > Nd > Pm > Sm > Eu > Gd > Tb > Dy > Y > Ho > Er > Tm > Yb > Lu > Sc > Al
Mixed	: Fe^{3+} > Al^{3+} > Ca^{2+} > Mg^{2+} > K^+ > Na^+ > H^+ > Li^+

Since the concentration of cations in a natural water sample would normally be quite low, the resin would seldom be saturated and the resin will normally pick up all of the ions in the solution. Only in very concentrated solutions will selectivity effects be noticeable.

Reproducibility and Minimum Detectable Limit

For any analytical method to be acceptable for quantitative work, the results that it gives must, of course, be reproducible. We find that the standard deviations for most ions are 5-10% when their concentrations are significantly above their detection limits. Such variation is typical for XRF analysis.

The limit of detection in x-ray spectrography is often used as 3 times the square root of the background counts. This is the method used to calculate the values listed in Table 6.

Standards

The calibration curves shown in Figures 4 and 5 were prepared by analyzing standard solutions made from analytical reagents. (These same standards were used to prepare all test solutions.) From the fitted curve taken from the data available, standard values for other elements can be determined. The experimental values along with concentrations used are listed in Table 6. Fitted values for the curves $\mu\text{g/cps}$ vs. At. No. are given in Tables 7 and 8.

Future Work

When working with As and Nb standards, it was found that neither of these were quantitatively picked up by the resin. The results were much different than expected and very non-reproducible. It was suggested that As is an anion in aqueous solutions and, therefore, might be picked up by an anion exchange resin. Quick tests were made using an anion exchange resin with the As and Nb

TABLE 6

At. No.	Element	$\mu\text{g/ml}$ Conc.	Filter	Line	Background CPS	Peak Intensity $\mu\text{g/CPS}$	% St. Dev.	MDL $\mu\text{g/g resin}$
20	Ca	40.2	Sn	$K\alpha$	8.454	2043 ± 290	14	570
20	Ca	40.2	Cu	$K\alpha$	5.204	80.3 ± 1.3	1.6	25
23	V	10.6	Sn	$K\alpha$	5.693	417 ± 7	1.7	95
23	V	10.6	Cu	$K\alpha$	4.652	27.4 ± 0.4	1.5	8
26	Fe	2.79	Sn	$K\alpha$	4.524	31.2 ± 1.1	3	6
28	Ni	3.30	Sn	$K\alpha$	2.668	24.1 ± 1.5	6	5
29	Cu	1.10	Sn	$K\alpha$	4.332	18.10 ± 0.9	5	4
30	Zn	1.85	Sn	$K\alpha$	3.982	14.2 ± 1.3	9	3
38	Sr	0.201	Sn	$K\alpha$	5.132	$4.17 \pm .18$	4	1.0
40	Zr	0.204	Sn	$K\alpha$	3.771	$1.98 \pm .26$	13	0.4
73	Ta	4.14	Sn	$L\alpha$	4.680	49.4 ± 2.5	5	10.0
80	Hg	2.09	Sn	$L\alpha$	4.872	28.2 ± 0.9	3	6.0
82	Pb	0.808	Sn	$L\alpha$	4.253	11.9 ± 0.5	4	3.0
92	U	0.400	Sn	$L\alpha$	3.651	4.52 ± 0.21	5	1.0

HIGH ENERGY RANGE

Table 7

XRF CALIBRATION

Sn Filter

35 kV - 30 mA

Integrated over 17 channels (= 0.32 keV)

K α Lines measured

<u>At. No.</u>	<u>Element</u>	<u>Obs. $\mu\text{g/cps}$</u>	<u>Fitted $\mu\text{g/cps}$</u>
20	Ca	2043	2311
22	Ti	-	489.4
23	V	417.	255.5
24	Cr	-	143.1
25	Mn	-	85.2
26	Fe	31.2	53.6
27	Co	-	35.4
28	Ni	24.1	24.4
29	Cu	18.1	17.5
30	Zn	14.2	13.0
31	Ga	-	9.96
32	Ge	-	7.86
33	As	Not Observed	6.36
34	Se	-	5.27
35	Br	-	4.46
37	Rb	-	3.39
38	Sr	4.17	3.04
39	Y	-	2.76
40	Zr	1.98	2.54
41	Nb	Not Observed	2.38

HIGH ENERGY RANGE

Table 8

XRF CALIBRATION

Sn Filter

35 kV - 30 mA

Integrated over 17 channels (= .32 keV)

L α Lines Measured

<u>At. No.</u>	<u>Element</u>	<u>Obs. $\mu\text{g/cps}$</u>	<u>Fitted $\mu\text{g/cps}$</u>
72	Hf	-	57.1
73	Ta	48.4	50.4
74	W	-	44.4
75	Re	-	39.1
76	Os	-	34.4
77	Ir	-	30.3
78	Pb	-	26.7
79	Au	-	23.5
80	Hg	28.2	20.7
81	Tl	-	18.2
82	Pd	11.9	16.0
83	Bi	-	14.1
84	Po	-	12.4
85	At	-	10.9
86	Rn	-	9.57
87	Fr	-	8.41
88	Ra	-	7.39
89	Ac	-	6.49
90	Th	-	5.71
91	Pa	-	5.01
92	U	4.52	4.40

standards, and it was found that Nb, but not As, was quantitatively removed. Another test was made using 0.5g anion exchange resin and 0.5g cation exchange resin in duplicate samples of tap water. The results were reproducible but did not compare with the results obtained using 1g of cation exchange resin. This looks like a promising possibility, and with more work, could develop into a feasible method. Work should be done to determine the best anion exchange resin and to see if reproducible results can be obtained.

Work should be done to compare the characteristics of the ion exchange resin beads to the Reeve-Angel ion exchange resin-loaded papers used by Campbell^{1.)}. Campbell's work was done by wavelength dispersive XRF, while this work was done by energy dispersive XRF. The results of both are impressive, but not comparable at this point. The resin-loaded papers have the advantage of being very thin, while the beads are bulky. Because of this, Campbell is able to report lower detectable limits than we are.

Applications

The suggested procedure was used to analyze 4 samples of tap water collected in the Pleasanton-Livermore area. Duplicate samples of the Pleasanton water showed good reproducibility and all of the samples contained the same elements in varying amounts. See Table 9.

TABLE 9
XRF ANALYSIS OF TYPICAL NATURAL WATERS
CONCENTRATIONS IN $\mu\text{g/ml}$

Elements	Sample No.					
	1	1(dup.)	2	3	4	4(dup.)
Ca(μg)	88.30	81.35	31.70	63.15	12.52	12.41
Fe	-	-	.379	-	-	-
Ni	.485	.451	.546	.482	.519	.539
Cu	.301	.266	.262	.246	.324	.321
Zn	-	-	.0787	-	-	-
Sr	1.490	1.248	.591	.835	.481	.483

#2
Nickel Adsorption on Ion Exchange Resin

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19

Linearity of Response for Ni Standards

#3 20
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8/8/1

FIGURE 34

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21

STANDARD CURVE FOR XRF USING ION EXCHANGE RESIN IN AQUEOUS SOLN.

100ml STANDARDS

1% CATION-EXCHANGE RESIN

AG 50W-X8

100-200 MESH

BID-RAD

K α LINES Sn FILTER

LITERATURE CITED

- 1) Campbell, W. J.; Spano, E. F., and Green, T. E. (1966), "Micro and Trace Analysis by a Combination of Ion Exchange Resin-Loaded Papers and X-ray Spectrography", Anal. Chem., Vol. 38, No. 8, P. 987-996.
- 2) Ryon, R. W., "Determination of Trace Impurities in Boron Carbide by Energy Dispersive X-Ray Fluorescence Spectrometry", UCRL 75108, Fig. 9.
- 3) U. Mertin, editor, "Desalinization by Reverse Osmosis", MIT Press, 1966, page 7.
- 4) Gordon, A. J., and Ford, R. A., (1972), "The Chemist's Companion: A Handbook of Practical Data, Techniques and References"; J. Wiley & Sons, New York, p. 383.

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