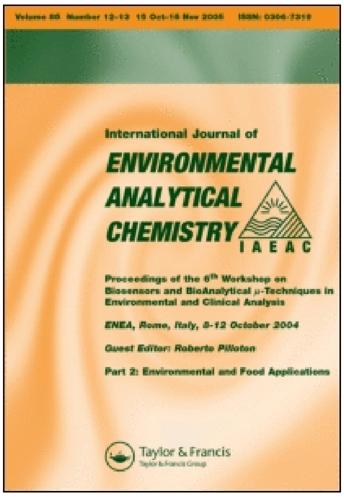


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Trace Metal Enrichment on Chemically Modified Filter Papers

G. Gendre[a]; W. Haerdi[a]; H. R. Linder[b]; B. Schreiber[b]; R. W. Frel[b]
[a] Department of Mineral, Analytical and Applied Chemistry, University of Geneva, Geneva-4, Switzerland [b] Analytical Research and Development, Pharmaceutical Department, Sandoz Ltd., Basel, Switzerland

To cite this Article Gendre, G. , Haerdi, W. , Linder, H. R. , Schreiber, B. and Frel, R. W.(1977) 'Trace Metal Enrichment on Chemically Modified Filter Papers', International Journal of Environmental Analytical Chemistry, 5: 1, 63 — 75
To link to this Article: DOI: 10.1080/03067317708071131
URL: http://dx.doi.org/10.1080/03067317708071131

Intern. J. Environ. Anal. Chem., 1977, Vol. 5, pp. 63–75
© Gordon and Breach Science Publishers Ltd., 1977
Printed in Great Britain

Trace Metal Enrichment on Chemically Modified Filter Papers

G. GENDRE and W. HAERDI

Department of Mineral, Analytical and Applied Chemistry, University of Geneva, 30 quai E. Ansermet, 1211-Geneva-4, Switzerland

H. R. LINDER, B. SCHREIBER and R. W. FREI

Analytical Research and Development, Pharmaceutical Department, Sandoz Ltd., 4002-Basel, Switzerland

(*Received March 4, 1977*)

KEY WORDS Trace metals, preconcentration, enrichment, thiocarbaminate filter papers, x-ray fluorescence, water analysis.

A trace enrichment technique for preconcentration of heavy metals on thiocarbaminate modified filter papers is described. The technique has been studied for Cu^{2+}, $Fe^{2+ \text{and} 3+}$, Zn^{2+}, Pb^{2+}, Ni^{2+}, As^{3+}, Sb^{3+}, Cd^{2+}, Hg^{2+}, VO^{2+} and UO_2^{2+}. Up to 100 μg of metal can be retained within one to two hours on the filter.

Effects of filter treatment of flow conditions and pH on filter capacity, filter permeability and recovery have been studied. Best recoveries were obtained in the pH range of 5–6. Considerable improvement on stability of the samples and reproducibility was achieved by subjecting the filters to high pressures prior to measurement. The technique was applied to the analysis of metal traces in ultra pure water samples (lower PPB range) and in organic samples by x-ray fluorescence.

INTRODUCTION

The determination of trace metals in the PPB concentration range in water samples can usually not be achieved without prior enrichment steps. For the measurement by x-ray fluorescence, atomic absorption or other techniques, the metal ions which are originally present in this dilution in 200–1000 ml of solution have to be fixed on a surface of about 1 cm^2 or contained in a volume of 1 to 2 ml. Simple evaporation techniques have the disadvantage of high risk of contamination from containers and laboratory surrounding. These can hardly be avoided in an average analytical laboratory when working with samples with such extreme dilution. Coprecipitation techniques are equally unqualified under such conditions.

Of interest are methods which employ chelating resins[1] or ion exchangers.[2] The metals are fixed to these materials by batch or column techniques. The use of ion exchanger paper or membranes for enrichment of ions in water samples has been known for some time.[3,4] The efficiency of such devices depends strongly on the salt concentration of the samples which limits their applicability.

Leyden *et al.*[5,6,7] have shown that this difficulty can be overcome by preconcentrating heavy metal ions from batch samples on silica gel modified with dithiocarbaminate. This worked in solutions with high salt concentration. The problem was the filtration and preparation of the metal containing silica gel for final measurement.

Knapp *et al.*[8] have transformed the ions into diethyldithiocarbaminates prior to adsorbtion on a column containing Chromosorb W-DMCS. The carbaminates were eluted with 2 ml chloroform onto a filter paper and the dryed paper disk exposed to x-ray fluorescence measurements. This procedure is still rather time consuming and a technique was desired whereby the enrichment and sample preparation steps could be combined into one.

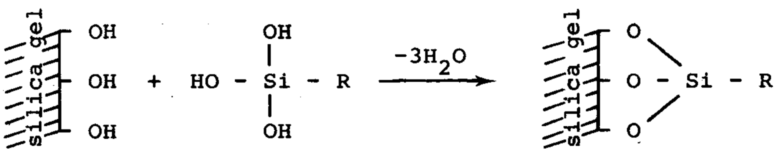
This study deals with the use of filter papers containing silica gel (Whatman SG 81) to which thiocarbaminate groups have been chemically bonded. In such a way the trace metals could be fixed on the paper by a simple filtration procedure.[11]

EXPERIMENTAL

Preparation of the filters[11]

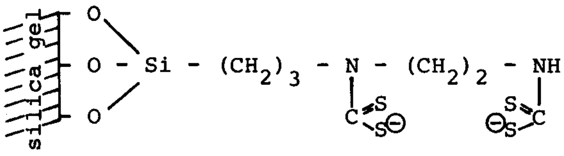
The silica gel contained in the Whatman paper SG 81 (Reeve Angel Ltd., London) is silylated with N-β-aminoethyl-aminopropyl-trimethoxysilane (Dow Corning Z-6020) according to the reaction below

$$\mathrm{R\text{-}Si\,(OCH_3)_3}\ \xrightarrow[\mathrm{H_2O}]{\mathrm{HAc}}\ \mathrm{R\text{-}Si\,(OH)_3 + 3CH_3OH}$$



$$\mathrm{R = -(CH_2)_3 - NH - (CH_2)_2 - NH_2}$$

This diamine is then treated with carbon disulfide to give the dithiocarbaminate below.



The resulting filter can be used as selective scavenger for heavy metal ions.

The silylation procedure is as follows: 25 ml silane Z-6020 are added to 100 ml methanol and stirred. After 5 min 50 ml 10% (v/v) acetic acid and after an additional 5 min 200 ml of water are added. Ten minutes later 75 ml of this solution are sprayed on a sheet of Whatman paper SG 81. This is followed by drying for 20 hrs at room temperature, washing with water and drying. After repeating this procedure filter disks of 13 mm diameter are cut from the sheet. These filters are dipped in a 1 N solution of complexone to eliminate traces of heavy metals, washed with water, dryed at room temperature and stored. Prior to actual use of the filters they are treated with CS_2. A solution is prepared with 20 ml iso-propanol, 4 ml NaOH (1N) and 600 ml water to which 10 ml of CS_2 is pipetted. This mixture is stirred for 5 min and 100 ml water are added. The filters are submerged in this solution and after 3 hrs removed and washed with water. In this form the filters are ready for use in the enrichment step. They may be stored for maximum 3 days in a refrigerator.

Enrichment step and measurement

The apparatus constructed for this enrichment technique is shown in Figure 1. A peristaltic pump Watson and Marlow MHRE 22 (Falmouth, England) permits to run 10 samples simultaneously. A filter holder (Millipore Swinnex Type SX 0001300) for 13 mm diameter filters and 50 ml sample containers made of polypropylene make up for the total instrument. For the enrichment step 50 ml of the acidic sample is treated with 1 ml 1 N acetate buffer (pH 5.3) and the pH adjusted to exactly 5.3 by adding ammonia solution. The sample is then filled into the sample container of one of the enrichment cycles. The pumping time is adjusted to permit at least 10 cycles for the total sample volume at a flow rate of 10 ml/cm^2 · min. Following this the filters are dryed, pressed for 20 sec at 40,000 kp with a pneumatic pellet press (Sa. Herzog, Osnabrück FRG; Type HTP 40) and fixed on Teflon disks of 50 mm diameter and 15 mm thickness for x-ray fluorescence measurement.

The measurement was done with a Siemens x-ray spectrometer SRS-1 equipped with a Cr-tube, a vacuumsystem, LiF-100-crystal, Ar-CH_4 gas flow counter and a sodium iodide scintillation counter.

The following measuring conditions were chosen for all the metals tested: x-ray tube operated at 55 kV and 40 mA; vacuum 0.3 torr; sample rotation; lithium fluoride crystal 100; 8 mm slit width; range 2.5V for count height analyzer, base line 0.66 V, channel width 0.50 V.

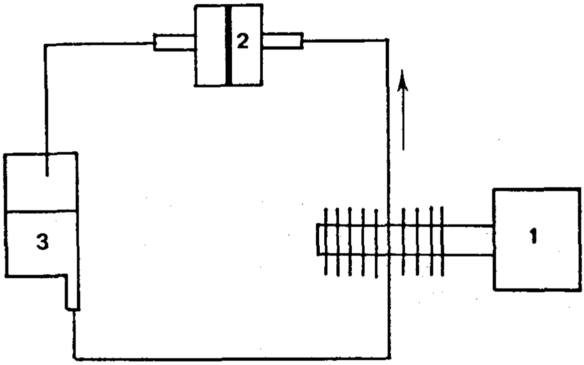


FIGURE 1 Schematic of the trace enrichment apparatus.
1) 10-channel peristaltic pump.
2) Filter holder and filter.
3) 50 ml sample container.

For lead and zinc the scintillation counter was used at 1133 V, for copper, nickel and iron the gas flow counter was used at 1567 V. Measuring angles for the lines (in degrees):

lead L_α	33.93	collimator 0.15°
zinc K_α	41.79	
copper K_α	45.02	collimator 0.40°
nickel K_α	48.66	
iron K_α	57.51	

The background was measured at 33.30°. The count rates for peak and background were divided and the quotient plotted as a function of metal concentration. Linear calibration functions were obtained.

RESULTS AND DISCUSSION

Capacity of filters

Iodometric titration was used to determine the total amount of dithiocarbaminate groups available. The procedure is as follows: The filter is dipped into a solution of 20 ml water and 4 ml iodine solution and the unreacted iodine backtitrated. Methylene blue is used as an indicator.

The titration results revealed a dithiocarbaminate content of 10.3 μmole/filter after a single treatment of the filter paper (see experimental section). Strictly additive values have been observed after dual and triple treatment.

A capacity of 5 μmole would theoretically result in a metal take up of approximately 300 μg assuming complete saturation. The actual capacities, however, are sometimes considerably below this value due to complexation equilibria and others. The percent recovery data for Cu, Fe, Ni, Pb and Zn in solutions of pH 7 and concentrations up to 200 μg are shown in Figure 2.

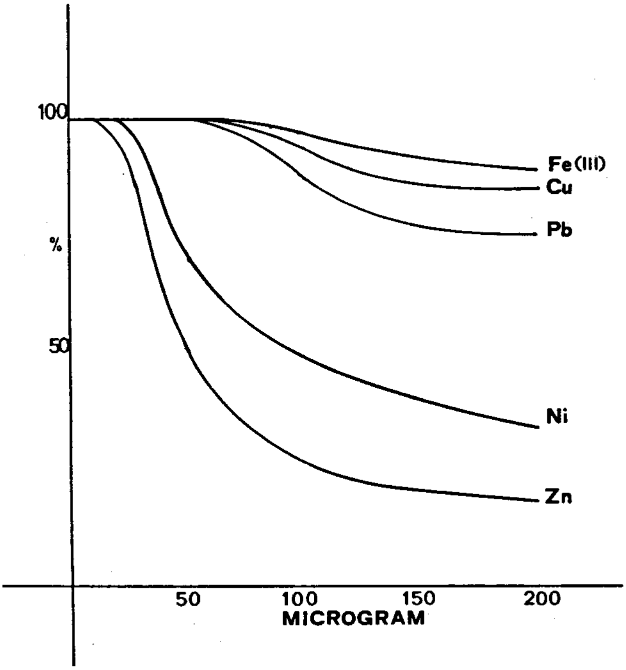


FIGURE 2 Capacity of the filters.

Up to 20 μg of Fe^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Ni^{2+} are quantitatively retained even in a mixture of all these metal ions. The behaviour of Co^{2+}, Fe^{2+}, VO^{2+}, UO_2^{2+}, Hg^{2+}, Cd^{2+}, As^{3+} and Sb^{3+} is similar. The ions AsO_4^{3-} and $Sb(OH)_6^-$ are only poorly retained and have to be reduced prior to enrichment.

Flow resistance of the filters

The permeability of the filters decreases with increasing volume of solutions passing the filter even without any metal ions being retained. This is attributed to a swelling effect. Another factor is the number of treatments with the silylation reagent. For an examination of these effects an aliquot of 50 ml of distilled water was passed through the filters at constant pressure and the time of the passage measured. The results are shown in Figure 3.

It is evident that subjecting the filters to a pre-swelling step overnight improves the permeability. It makes a difference whether the swelling occurs in static condition or under pressure and flow conditions. The decrease in permeability as a function of the number of silylations is also drastic and limits the number of silylation steps to maximum two for practical reasons.

pH-dependence of the enrichment procedure

The pH profile was measured with solutions of the following composition:

—2,5 g anhydrous sodium sulfate specially purified (to stimulate the salt content of the sample digestion),
—10 μg each of the metals Fe^{3+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}.
—1 ml buffer solution. A piperazine/HNO_3 buffer was used for the pH range 5–6 and triethanolamine/HNO_3 for the pH range 7–8.
—This was filled up to 25 ml with doubly distilled water.

The results are shown in Figure 4. It can be seen that the yields for Zn drop drastically at higher pH. All further experiments were therefore carried out between pH 5 and 6 using a buffer solution of 1 M sodium acetate in acetic acid.

Speed of enrichment step

10 ml of solutions containing each 33 μg Fe, Cu, Ni and Zn were subjected to the enrichment procedure at pH 5.1 adjusted with a 1 M acetate buffer. The metal concentration as a function of time was monitored by ASS. The total salt content of the solution was kept at 100 g Na_2SO_4/1. Figure 5 contains the results. With recycling times of more than three hours the metal complexes seem to redissolve slowly hence the efficiency of the enrichment procedure decreases. The phenomenon can be attributed to CS_2 splitting from the complex and to oxydation. Based on these data the optimal enrichment time is between 1 and 2 hrs.

Calibration function and detection limits

The calibration functions were studied under the optimal conditions mentioned above. Solutions (10 ml each) containing 10, 20, 50, 100 and 200 ug

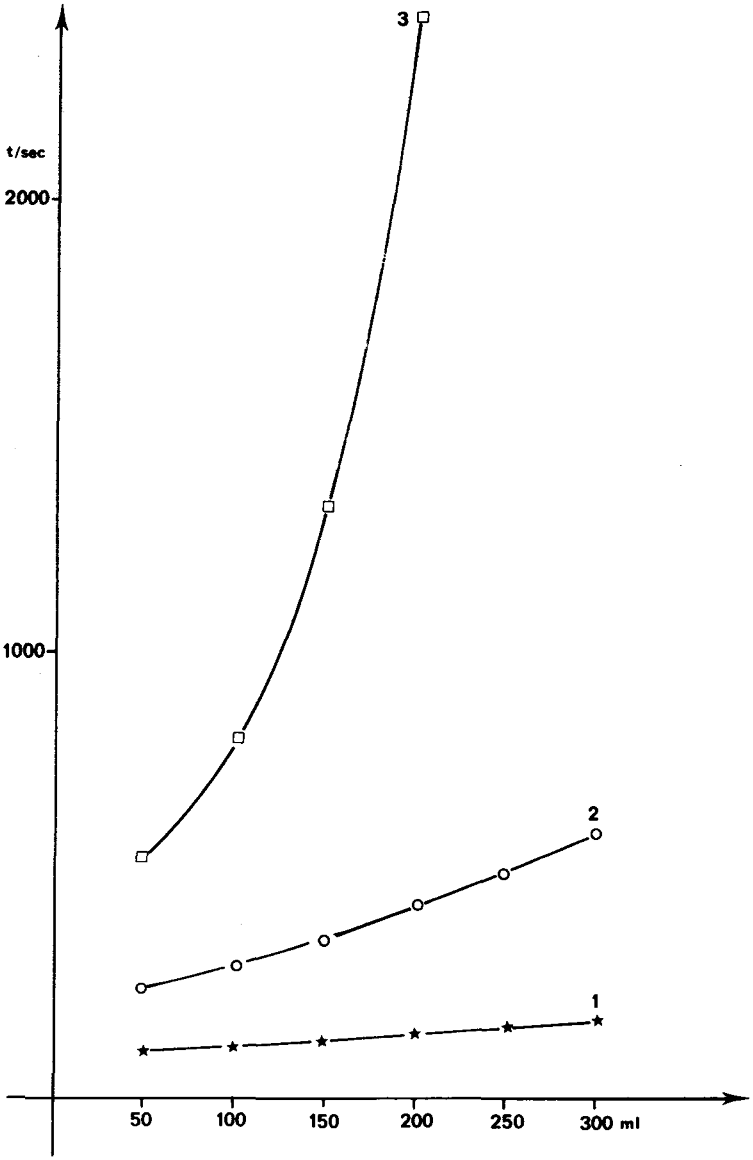


FIGURE 3 Permeability of different filters measured as the time needed to pump a certain volume through the filter at a constant pressure.

1) Filter with one silylation treatment and pre-swelling for 12 hrs under static condition.
2) One silylation treatment, no pre-swelling.
3) Two silylation treatments, no pre-swelling.

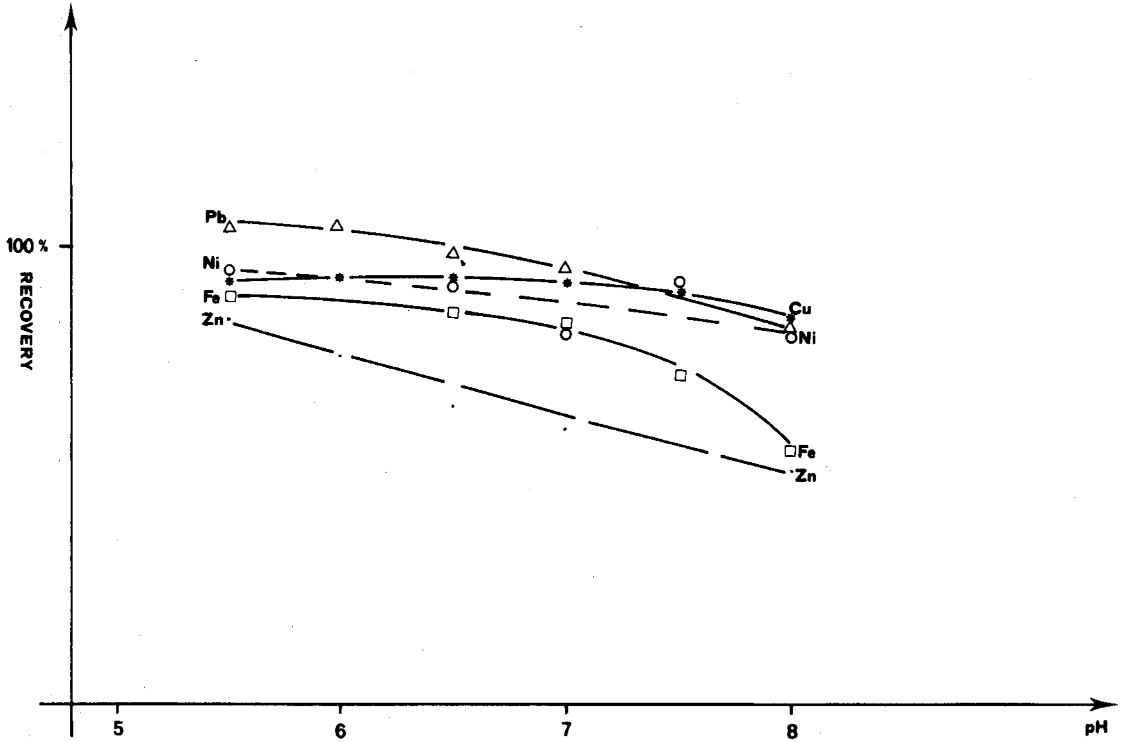


FIGURE 4 pH-profile; the % recovery as a function of pH.

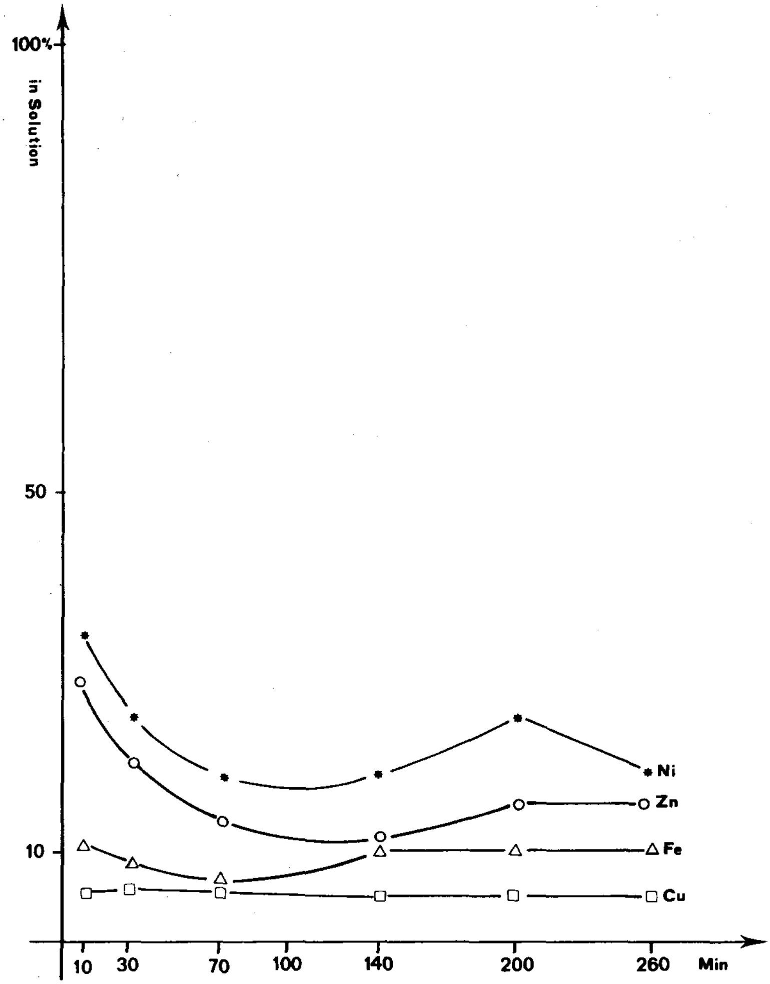


FIGURE 5 Influence of time of the enrichment procedure on the recovery of the metals from a solution containing 33 μg of each metal (pH 5).

of each metal (Cu, Fe, Zn, Pb, Ni) plus a blank were enriched according to the discussed procedure and measured by x-ray fluorescence. Another solution containing only Zn and Ni was treated alike.

The data including slope values, regression coefficient and detection limits are compiled in Table I and Figure 6. It can be seen clearly that the total amount of metal in the solution exerts a strong influence on the linearity of the calibration function of each metal. Generally it can be said that a total metal concentration of up to 50 μg/filter assures a regression coefficient of 0.9999 for a concentration range of up to 20 μg and results in detection limits below 1 PPM.

The detection limits given in Table I are reported as real detection limits Cg computed according to Plesch.[9] It is the limiting concentration which can be measured and distinguished with 99.7 % certainly from zero.

It contains all the errors from sample preparation, instrumental errors and errors of the count statistics.

TABLE I
X-ray fluorescence calibration data and detection limits

Element	Slope 0–20 μg	Regression 0–20 μg	Detection limit[9] (μg)
Copper	54	0.998	3
Zinc	57	0.978	11
Lead	5	0.999	2
Nickel	58	0.999	3
Iron	56	0.998	4
Zinc	55	0.99998	0.4
Nickel	65	0.99999	0.2

APPLICATIONS

Ultra trace analysis in distilled water samples

In this study the water quality of different distillation apparatus had to be investigated. This included a larger distillation facility in an ampoule filling station, a single distillation unit with Teflon coated glass and a double distillation quartz unit. The samples were examined for traces (PPB) of Fe, Zn, Cu and Ni. The use of efficient trace enrichment techniques was absolutely essential. Here the described filtering technique and as a comparative method partial evaporation and coprecipitation with Na-dibenzyldithiocarbaminate[10] was used. Particularly for the latter technique extreme care had to be taken to avoid contamination.

Decontamination of the polypropylene sample flasks which served originally as containers for ultra pure hydrochloric acid were washed three times with a 0.1 N EDTA-solution and hot, bidestilled water. The same washing procedure was applied to all the parts of the enrichment apparatus in contact with sample solution. One liter each of the distilled water samples were

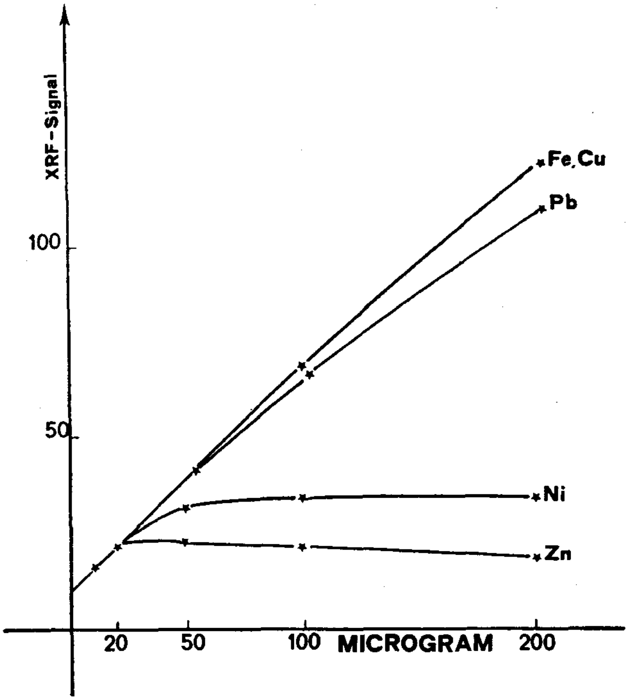


FIGURE 6 Calibration functions for some metals, following the trace enrichment step. Measurements by x-ray fluorescence.

collected directly at the outlet of the distillation apparatus. Within 10 min from sampling time 150 ml aliquotes were taken and mixed with 1 ml triäthanolamine/HNO_3-buffer and cycled through the filter. Another aliquot of 150 ml was evaporated overnight (12 hrs) in a teflon beaker to which 1 ml aqua regia had been added. The residue was neutralized, buffered with acetate buffer to pH 4 and precipitated from about a 40 ml volume with dibenzyldithiocarbaminate, filtered, dried and evaluated. Sample measurement was carried out by x-ray fluorescence. The results are shown in Table II.

The high results obtained for iron when using the coprecipitation procedure can be attributed to contamination during the evaporation process. Otherwise there is good agreement between the two enrichment techniques. The advantages of the filter technique is obvious for this type of problem.

Trace analysis in different organic matrices

Ten different organic samples (dyes, active principles, excipients etc.) were digested conventionally with a H_2SO_4/HNO_3-mixture and again enriched by

TABLE II

Comparative concentrations of trace metals (in PPB); a) Filtration technique; b) coprecipitation

Distillation apparatus	Copper		Nickel		Iron		Zinc	
	a)	b)	a)	b)	a)	b)	a)	b)
1	<1	<2	<3	<5	3–6	<5	<2	<5
1	<1	<2	<3	<5	3–6	16	<2	<5
2	<1	<2	<1	<5	12	23	<1	<5
3	<2	<2	<1	<5	3–6	<5	3–6	<5

1. High capacity glass apparatus, single distillation.
2. Glass apparatus.
3. Quartz apparatus, double distillation.

the two above mentioned techniques. Agreement between the two methods was satisfactory. The concentration range studied was in the sub and lower PPM region. Contamination problems resulting from glass ware and reagents used for digestion can be quite serious.

CONCLUSIONS

The trace enrichment technique for heavy metals on thiocarbaminate modified filter paper shows promise for the analysis of high purity water samples and for preconcentration from large volumina of alkali salt solution as encountered when digesting organic samples.

Up to 100 μg total metal content can be retained on the filter within one hour. When working under the optimal conditions mentioned in this paper, the method is applicable to Cu, Fe, Zn, Pb, Ni, As, Sb, Cd, Hg and V in the oxydation states mentioned before.

It should also be possible to use this technique for heavy metal analysis in waste water effluents. A limiting condition at this time is, however, that none of the metals indicated should be present in large excess due to capacity reasons. For example, for strongly iron containing samples it would be difficult to use this technique and its feasibility should be tested with small volumes (up to 5 ml) first. Further work on this problem is undertaken.

In general one can say that the filter enrichment approach proposed in this paper has several advantages in comparison to other preconcentration techniques such as extraction, coprecipitation and evaporation. They can be summarized as follows:

—short concentration times
—completely closed system and hence little danger for contamination
—minimal reagent consumption which again reduces contamination
—no further sample preparation is needed prior to measurement
—simple handling and small actual working time.

References

1. K. F. Sugaware, H. H. Weetall, D. G. Schucker, *Anal. Chem.* **46,** 489 (1974).
2. C. W. Blount, D. E. Leyden, T. L. Thomas and S. M. Guill, *Anal. Chem.* **45,** 1045 (1973).
3. W. J. Campbell, E. F. Spano, T. S. Green, *Anal. Chem.* **38,** 987 (1966).
4. C. L. Luke, *Anal. Chem.* **36,** 318 (1964).
5. E. Leyden, G. H. Luttrel, T. A. Patterson, *Analytical let.* **8**(1), 51 (1975).
6. E. Leyden and G. H. Luttrel, *Analytical Chemistry* **47**(9), 1512 (1975).
7. E. Leyden, G. H. Luttrel, W. K. Nonidez, D. B. Werho, *Analytical Chemistry* **48**(1), 67 (1976).
8. G. Knapp, B. Schreiber, R. W. Frei, *Anal. Chim. Acta* **77,** 293 (1975).
9. G. Plesch, Siemens-Analytische Mitteilung Nr. 84 (Siemens Aktiengesellschaft, Postfach 211080, 7500 Karlsruhe, GRF).
10. B. Schreiber *et al.*, *Anal. Chem.* (to be submitted).
11. G. Gendre, Préparation et étude de complexants solides, Univ. Genève 1976 (paper in preparation).