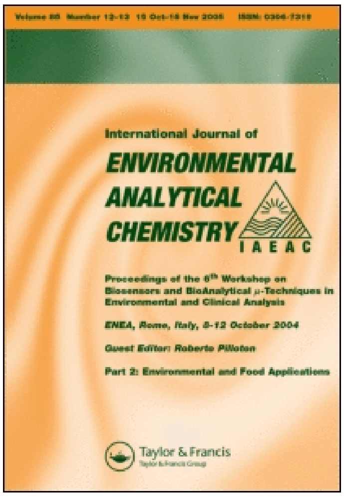

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The Effect of Naturally Occurring Organic Materials Upon the Preconcentration of Metal Ions and Upon Their Determination by Spectrometry

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The effects of humic and fulvic type organic materials on the determination of trace metal ions by inductively coupled plasma emission spectrometry (ICP), direct current plasma emission (DCP), atomic absorption (AA) and several methods of preconcentration prior to X-ray spectrometric determination was investigated. The ICP, DCP and AA methods showed little or no serious effect, whereas problems of various severity were noted in the cases of the preconcentration methods. In almost all cases, a 15 min. irradiation with ultraviolet radiation improved or at least caused no detriment to the results. An exception was to affect the oxidation state of arsenic.

KEY WORDS: Metal ions, organics, water, ICP, DCP, AAS, XRF, humic acids, fulvic acids, preconcentration.

INTRODUCTION

Several methods have been investigated and evaluated in this laboratory for the pre-concentration of trace amounts of environmentally significant elements in water. These methods are precipitation by sodium diethyldithiocarbamate[1] or ammonium pyrrolidinedithiocarbamate[2] with collection on a membrane filter, complexation by 8-hydroxyquinoline with adsorption on activated carbon,[3] filtration through an ion exchange resin impregnated filter paper[4] and chelation by a dithiocarbamate immobilized on controlled pore glass.[5] The above methods were chosen for their ability to

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preconcentrate trace amounts of many elements into a thin film sample suitable for simultaneous multielement determination by energy dispersive X-ray spectrometry. On application of the above methods to the analysis of natural waters, significant detrimental effects such as unfilterable colloids and reduced recoveries were encountered. These effects are in part a consequence of the presence of so-called "humic" materials which are commonly found in natural waters and arise from the natural decomposition of vegetable matter.[6] Such materials are considered to be high molecular weight polymers containing aromatic rings highly substituted with both phenolic and carboxylic functional groups[7,8] and have been shown to form complexes with a number of environmentally important metals.[9,10] This study demonstrates the influence of humic materials upon preconcentration methods and the ability of photochemical oxidation to remove the observed effects.

EXPERIMENTAL

Instrumentation

Energy dispersive X-ray fluorescence spectra were obtained using a Spectrace 440 spectrometer (United Scientific Corporation, Mountain View, CA) equipped with a silver anode X-ray tube and a lithium drifted silicon semiconductor detector. The X-ray tube was operated at 30 kV, 0.30 mA in the pulsed mode using a 0.025 mm silver foil filter. Counting time was 200 sec per sample; counts were collected and processed by a multi-channel analyzer (TN-880, Tracor Northern, Middleton, WI) interfaced to a PDP 11/05 computer (Digital Equipment Corp., Maynard, MA). The atomic absorption spectrometer was a Perkin Elmer Model 303 (Perkin Elmer Corp., Norwalk, CT) equipped with a three slot burner and hollow cathode lamps supplied by the instrument vendor. The inductively coupled plasma optical emission spectrometer (Model QA 137, ARL, Sunland, CA) used an all-argon plasma and a direct reading polychromator. The d.c. plasma optical emission spectrometer (Spectraspan III, Spectrametrics, Andover, MA) was operated with an argon plasma and a direct reading polychromator.

Apparatus

Ultra violet irradiation of samples was accomplished at 254 nm using six 130 cm^3 quartz tubes positioned radially 3 cm distance from a 550 W medium pressure mercury arc lamp (Hanovia, Ace Glass, Vineland, NJ).

Reagents

Metal standard solutions ($1000\,mg\,l^{-1}$) were prepared in 1% v/v HNO_3 from the nitrate or pure metal wherever possible. The humic and fulvic acids were prepared from Irish peat by extraction and purified by dialysis. The precipitating reagents, sodium diethyldithiocarbamate and ammonium pyrrolidinedithiocarbamate were prepared as 0.1 and 1% w/v aqueous solutions respectively. 8-hydroxyquinoline was prepared as a $150\,mg\,l^{-1}$ solution in acetone. Activated carbon (Merck) was treated first with concentrated HF and then with concentrated HCl (72 hours each) before finally washing with boiling deionized water and drying. Ion exchange resin impregnated filter papers (SA-2, Whatman, Clifton, NJ) were prewashed with saturated brine to ensure the presence of the exchanger in the Na^+ form. Controlled pore glass (CPG-10, Electronucleonics, Fairfield, NJ) was supplied as 200–400 mesh particles having a nominal particle diameter of 75 Å, pore volume of $4.0\,ml\,g^{-1}$ and a surface area of $110\,m^2\,g^{-1}$. The glass was derivatized using a previously published method and its subsequent capacity for copper was determined ($0.5\,mmol\,g^{-1}$).

METHODS

a) *Dithiocarbamates:* Samples were adjusted to pH 4, buffered with $10\,cm^3$ 0.1 M KH_2PO_4 (pH 4) and $5\,cm^3$ precipitating reagent added. After stirring (5 mins) and aging (20 mins) the precipitates were collected on a 0.45 μm membrane filter (Gelman GA-6, Gelman Sciences, Inc., Ann Arbor, MI). The filters were air-dried and mounted between 0.0006 mm Mylar films (Chemplex Industries, E. Chester, NJ).

b) *Chelation by immobilized dithiocarbamate:* Samples were adjusted to pH 6 with 0.4 M NaOH and $10\,cm^3$ 0.1 M K_2HPO_4 buffer solution added. The resulting samples were passed through columns containing 200 mg of the derivatized glass at a flow rate of $30\text{–}40\,cm^3\,min^{-1}$. The column packing was then removed, dried for 10 hours in a vacuum desiccator, homogenized and mounted between Mylar films.

c) *Complexation with 8-hydroxyquinoline and adsorption on activated carbon:* Samples were adjusted to pH 8 and $10\,cm^3$ 0.1 M ammonia/ammonium chloride buffer (pH 8) added. $1\,cm^3$ $150\,mg\,l^{-1}$ 8-hydroxyquinoline in acetone solution was then added followed by 100 mg activated carbon. The resulting solution was placed in a glass container on a rolling pot mill for 1 hour before filtering through a 0.45 μm membrane filter. The filters were mounted while moist on X-ray cups using Mylar film to support both sides of the activated carbon.

d) *Resin impregnated filter papers:* Samples were adjusted to pH 3 and 2 cm^3 0.003 M KH_2PO_4 buffer (pH 3) added. The solution was then filtered seven times through the same filter paper to ensure complete removal of metal ions. The filter disk was then mounted between Mylar sheets for X-ray analysis.

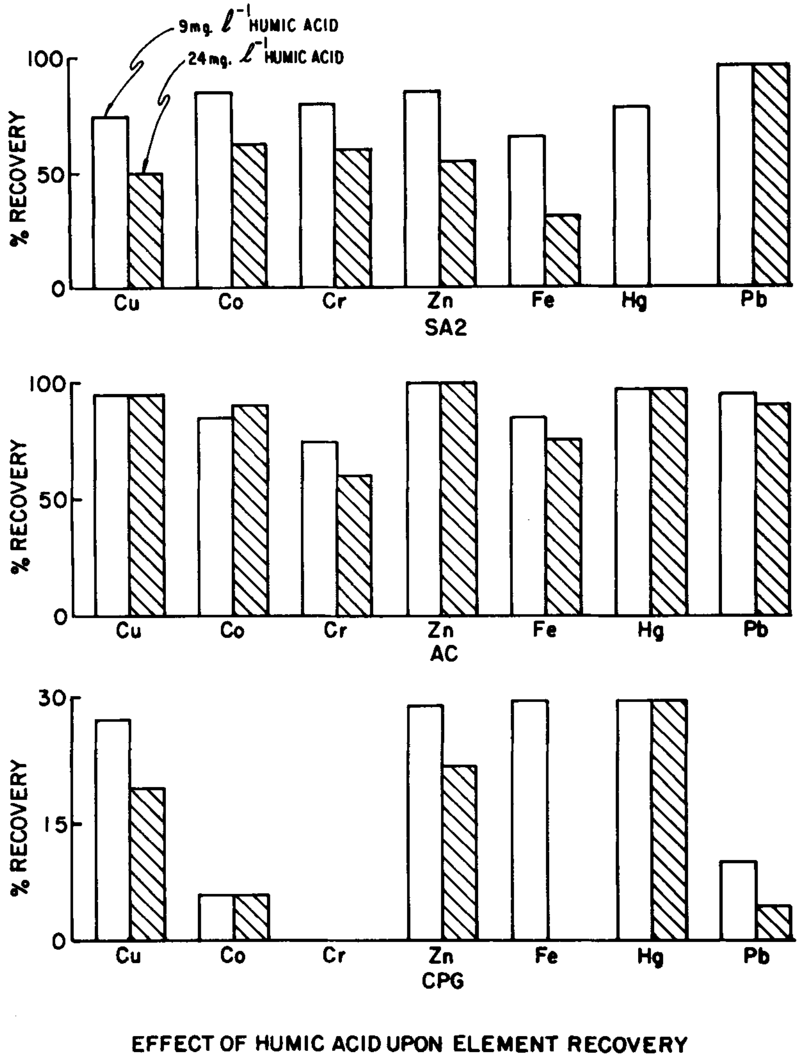
RESULTS AND DISCUSSION

Pilot Study

Initially, it was necessary to identify the type and magnitude of the effect of humic materials upon the preconcentration methods. Thus, five replicate determinations were made for each of the ions Co(II), Cr(III), Cu(II), Zn(II), Fe(III), Hg(II) and Pb(II) using each of the preconcentration methods described above. Three solutions containing 200 $\mu g\,l^{-1}$ metal ion alone, 200 $\mu g\,l^{-1}$ metal ion + 9 $mg\,l^{-1}$ humic acid, and 200 $\mu g\,l^{-1}$ metal ion + 24 $mg\,l^{-1}$ humic acid respectively were employed. The effect of both levels of humic acid upon the sodium diethyldithiocarbamate and ammonium pyrrolidinedithiocarbamate precipitation methods was to form a filter-clogging colloid rendering the methods impractical. The effect of humic acid upon the remaining three preconcentration methods is summarized in Figure 1 in which recoveries of each metal, by each method and for both levels of humic acid are normalized to the recovery of metal in the absence of humic acid. It is noticeable that the method using 8-hydroxyquinoline/activated carbon is least affected; presumably due to the adsorption of any humic-metal complexes along with the oxine complexes onto the activated carbon.[3] The resin impregnated filter paper shows proportionate lowering of recovery at the two levels of humic acid for all ions except Pb(II), suggesting formation of non-exchangeable metal-humic complexes in the case of most ions. The controlled pore glass-immobilized dithiocarbamate method was found to exhibit significantly decreased recoveries ($\leq 30\%$ relative) for all elements. This decrease may result from the formation of metal-humic complexes and/or from coating of the silylated surface by adsorption or plugging of the pores. It may be concluded from the pilot study that humic material interferes with the preconcentration of most ions investigated and that methods for the removal of this interference must be sought if preconcentration is to be employed.

Methods for the elimination of humic interferences

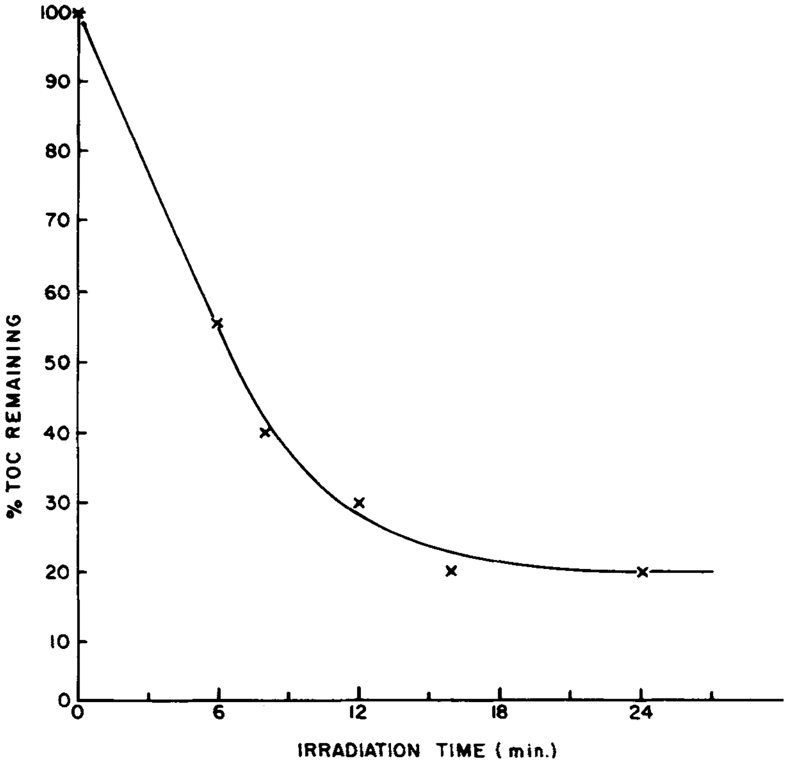
Three methods for eliminating humic interference prior to metal



EFFECT OF HUMIC ACID UPON ELEMENT RECOVERY

FIGURE 1 Percentage recoveries of Cu(II), Co(II), Cr(III), Zn(II), Fe(III), Hg(II) and Pb(II) in the presence of 9 and 24 mg l^{-1} of humic acid. (A) Ion-exchange resin impregnated filter paper, (B) Oxinate adsorption on activated carbon, (C) Dithiocarbamate immobilized on controlled pore glass.

concentration were considered. These were adsorption on activated carbon,[3] wet oxidation using either dichromate,[12] permanganate[13] or persulphate[14] and photochemical decomposition.[15] The use of adsorption on activated carbon creates sample handling difficulties. Use of wet



DESTRUCTION OF ORGANIC MATTER IN WATER BY UV IRRADIATION

FIGURE 2 Total organic carbon as a function of UV irradiation time in the presence of the trace elements.

oxidation was also discounted because of inefficiency, speed and the inevitably increased blanks arising from reagent addition. Thus, UV irradiation was chosen because no additional reagent is required and rapid degradation of organics with only water and carbon dioxide as by-products is possible. The concentration of total organic carbon of a solution containing both humic and fulvic acids (5 ppm each) as a function of UV irradiation time is shown in Figure 2. Substantial degradation of organic material is achieved after 15 minutes irradiation with the solution adjusted to pH 2. The ability of ultraviolet (UV) irradiation to reduce the effects attributable to humic materials was investigated using four types of solution:

O containing 200 μg l^{-1} metal ion only.
H containing 200 μg l^{-1} metal ion + 9 mg l^{-1} humic acid.
F containing 200 μg l^{-1} metal ion + 5 mg l^{-1} fulvic acid
and
M containing 200 μg l^{-1} metal ion + 5 mg l^{-1} humic + 5 mg l^{-1} fulvic acid.

Each of these solutions contained 200 μg/l^{-1} of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Hg(II), Pb(II), Cd(II), As(III) and Tl(I) which were determined with no pretreatment and after UV irradiation for 15 minutes at pH 2.

Dithiocarbamate precipitation

In the absence of UV irradiation, both sodium diethyldithiocarbamate (NaDDTC) and ammonium pyrrolidinedithiocarbamate (APDC) yielded unfilterable colloids in the presence of humic acid and mixed humic/fulvic acid solutions. Fulvic acid alone similarly affected NaDDTC while APDC was unaffected for all the ions considered in that case [Fe(III), Co(II), Ni(II), Cu(II), Zn(II), As(III), Pb(II) and Hg(II)]. After UV irradiation of the four types of solution, essentially quantitative recovery of all the elements determined was obtained with the exception of As(III). The results indicated a severe loss of recovery of As(III) after UV irradiation. This loss was independent organic content and may have been a result of the oxidation of As(III) to As(V) during irradiation. As(V) is not precipitated by either dithiocarbamate.

Dithiocarbamate immobilized upon controlled pore glass

Severe depression of recovery in the presence of humic material had been encountered in the pilot study and was observed in the extended study as shown in Table I. Significant decreases of recovery were observed for Cr(III), Mn(II), Fe(III), Cu(II), Hg(II) and Pb(II) when humic, fulvic or both acids were present. Only the presence of the mixed organic solution decreased the recovery of Co(II), Ni(II), Zn(II) and Tl(I) significantly. Without exception, the recovery was restored to nearly 100% after UV irradiation, demonstrating the potential utility of this method for degradation of the organic material.

TABLE I

Effect of organics and irradiation on the relative recoveries[a] of selected elements by the CPG method

	Untreated			Irradiated		
	H	F	M	H′	F′	M′
Co	94	97	81	92	96	96
Ni	95	93	75	93	105	93
Zn	96	86	79	104	106	91
Tl	112	99	89	96	99	101
Cu	86	85	66	98	98	97
Cr	31	92	19	93	87	105
Mn	46	72	38	118	83	86
Fe	41	84	27	96	105	106
Hg	52	59	51	97	101	90
Pb	45	69	24	98	101	92

[a] Percent relative to identical samples with no added organics.

Ion exchange resin impregnated filter paper

The use of this method was particularly advantageous for the ions recoverable (Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Hg(II) and Pb(II)) as there was no significant loss of recovery in the presence of either or both humic and fulvic acid. Thus, there was no need for UV irradiation at the organic levels considered although irradiation gave no loss of precision and, therefore, might be of use if organic levels were high enough to require their removal.

Complexation by 8-hydroxyquinoline and adsorption on activated carbon

For the elements considered (Mn(II), Cr(III), Zn(II), Fe(III), Ni(II), Cu(II), Co(II), Pb(II) and Hg(II)) there was no significant loss of recovery in the presence of humic or fulvic acid or of their mixture. This may be attributed to the adsorption of any metal-humic complexes on the activated carbon.[3] There was, therefore, no advantage to be gained from UV irradiation of the samples at the levels of organic material considered.

Effects of humic material upon other spectroscopic techniques

A parallel study to that using preconcentration and energy-dispersive XRF was conducted using flame atomic absorption (AAS), d.c. plasma optical emission (DCP/OES) and inductively coupled plasma optical emission (ICP/OES) spectrometry. Aliquots of the four sets of solutions (O, H, F and M) used for the X-ray studies were used for the determination of each element possible both before and after UV irradiation. None of the three methods yielded a significant depression of signal due to humic materials. There was no significant variation between irradiated samples and those which were not irradiated.

Arsenic

Arsenic was an element whose behavior on irradiation and subsequent determination by energy-dispersive XRF after dithiocarbamate precipitation was anomalous. Irradiation was found to decrease the recovery to less than 20% of the expected value as shown in Table II. Results from the analysis of aliquots of the same samples using DCP/OES and ICP/OES show no such decrease as shown in Table III. From the DCP/OES and ICP/OES results it is clear that total As is unaffected by the presence of humic materials or by irradiation, and is therefore not being lost as a volatile arsenic compound. On irradiation of the sample in nitric acid solution at pH 2 it appears that the As present does not yield a precipitate with the dithiocarbamates. This likely results from the oxidation of As(III) to As(V); the latter does not form precipitates with dithiocarbamates.

TABLE II

Effect of UV irradiation upon the recovery (%) of 20 μg As by two precipitation methods

	Untreated				Irradiated			
Method	0	H	F	M	0′	H′	F′	M′
APDC	100	[a]	102	[a]	10	8.5	9.8	6.9
NaDDTC	100	[a]	[a]	[a]	10.7	21.6	14.3	13.7

[a] Forms an unfilterable colloid.

TABLE III
Effect of UV irradiation upon the recovery (%) of 20 μg As by various techniques.

Method	Untreated Ø	H	F	M	Irradiated Ø′	H′	F′	M′
APDC EDXRF	100	[a]	102	[a]	10	8.5	9.8	6.9
NaDDTC EDXRF	100	[a]	[a]	[a]	10.7	21.6	14.3	13.7
ICP/OES	100	96.6	97	95.3	99.2	91.1	94.9	98.7
DCP/OES	100	106	112	108	89	106	102	109

[a] Forms an unfilterable colloid.

CONCLUSIONS

Of several methods available for the preconcentration of trace metal ions prior to determination using energy-dispersive XRF spectrometry, complexation with 8-hydroxyquinoline followed by adsorption on activated carbon and collection on an exchange resin impregnated filter paper are generally unaffected by humic substances at concentrations of 10 ppm or less. Methods employing precipitations by NaDDTC and APDC or complexation by an immobilized dithiocarbamate on the other hand, show severe loss of efficiency in the presence of dissolved humic material. The efficiency of these methods may be simply and reliably reinstated by UV irradiation of the sample for 15 min at pH 2. Such treatment should alleviate difficulties often encountered in the analysis of natural waters high in humic substances.

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