Table IV Recoveries of Nitro-Substituted Compounds Spiked into Water at the 4 μg/L Level Using 60–80 Mesh XAD-4

compd	% recovery	compd	% recovery
NB	97 ± 7[a]	1,3,5-TNB	98 ± 5
1,3-DNB	99 ± 3	2,4,6-TNT	97 ± 3
2,6-DNT	99 ± 6	RDX	97 ± 5
2,4-DNT	98 ± 6		

[a] Standard deviation calculated from four to six runs.

Table V. RDX in Groundwaters by Three Different Procedures

	amt of RDX, μg/L		
ground-water no.	CH_2Cl_2 extraction	XAD-2	XAD-4
1	23	13[a]	24
2	35	22	40
3	29	14	30
4	0.8	0.7	1.6
5	42	29	47
6	13	6.2	15
7	ND[b]	1.0	1.8

[a] All values uncorrected for recovery efficiency. [b] ND, not determined.

formation of microparticles of the test compounds is the probable cause of low recoveries. The exact explanation for higher recoveries when smaller mesh resin is used cannot be given from existing data, but the probable reason is effective filtration of microparticles of the test compounds combined with more efficient contact of the test compounds with exposed resin surfaces. Our preliminary data using XAD-2 and XAD-4 of different shapes and sizes lend support to incomplete dissolution being the explanation for low recoveries of some compounds when solid sorbents are used for the extraction.

Field Sample Results. RDX was extracted from groundwater samples taken from monitor wells at a munition disposal site. The traditional solvent extraction with CH_2Cl_2 and extraction by the resin sorption procedure were employed using both 20–50 mesh XAD-2 and 60–80 mesh XAD-4. Results are given in Table V. The lower results, using XAD-2, confirm the ~65% recovery established from tests of con-

trived samples. The agreements of the XAD-4 and the CH_2Cl_2 solvent extraction results for these field samples, and the nearly 100% recovery when XAD-4 was used for contrived samples, establish the validity of the resin sorption procedure as described in this report.

CONCLUSION

The test data for contrived samples and the results given in Table V for field samples show that 60–80 mesh XAD-4 can be used to determine accurately the nitrated organic compounds in environmental waters. The same results are obtained as those for use of the recommended methylene chloride extraction, but with much less time per determination and at very reduced solvent and transportation costs.

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Characterization of Functional Group Complexation of a Poly(dithiocarbamate) Chelating Resin

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Alteration of chelating efficiency of a poly(dithiocarbamate) resin caused by thiocyanate contamination was evaluated for transition metals. The resin capacity for Cu, Co, and Fe(III) was inversely related to the thiocyanate concentration. When synthesized by the reaction of carbon disulfide and a poly-amine–polyurea resin in pyridine instead of ammonium hydroxide, the resin capacity was maximized by elimination of thiocyanate.

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The poly(dithiocarbamate) (PDTC) resin is effective as a chelate ion exchanger for separation and preconcentration in trace analyses with atomic spectroscopy (1, 2). The resin is formed by the reaction of carbon disulfide with a poly-amine–polyurea resin (3). Infrared spectra of the poly(dithiocarbamate) resin indicated the presence of both dithiocarbamate and isothiocyanate groups. However, direct analysis failed to establish the actual dithiocarbamate content. The existence of an inner salt structure as opposed to the expected ammonium salt was inferred from the ammonium concentration (4). When the resin capacity was determined

Table I. Wavelengths for ICP-AES and Figures of Merit

element	wavelength, nm	detection limit,[a,b] ng/mL
Cu	324.7	6
Co	238.9	10
Fe	238.2	20

[a] Calculated from 3 times the standard deviation of the background. [b] Continuous nebulization.

by the use of batch equilibration, it varied considerably from metal to metal (3).

The poly(dithiocarbamate) resin functionality has not been characterized extensively. Hackett presumed that the isothiocyanate groups were formed on the resin as a result of oxidation of primary dithiocarbamate groups (4). As the iodometric titration of the dithiocarbamate group was not possible, thiocyanate was presumed to interfere with the iodometric end point. The presence of thiocyanate on the resin was proven first in this investigation with a qualitative test by the use of the reaction of Fe(III) solution. Many batches of poly(dithiocarbamate) resins have been prepared since the material was described originally, and all of them prepared with the method described by Hackett and Siggia (3) showed the red Fe(III) thiocyanate reaction. Furthermore, these resins exhibited an IR absorption between 2150 and 2000 cm⁻¹ characteristic of the isothiocyanate (—N=C=S) or thiocyanate (—S—C≡N) stretching. The thiocyanate ion coordinates some metals through the sulfur free electron pair (thiocyanateo-) but others by the nitrogen electron pair (isothiocyanate complex) (5). The thiocyanate observed in the poly(dithiocarbamate) resin IR spectrum appeared to have reacted with Fe(III) to form red thiocyanato complexes.

The determination of thiocyanate content, its role in poly(dithiocarbamate) resin complexation, and preparation of a thiocyanate-free poly(dithiocarbamate) resin are described in this report.
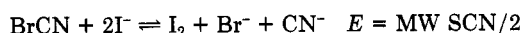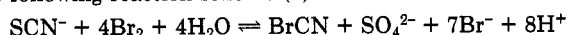
EXPERIMENTAL SECTION

Apparatus. The inductively coupled plasma (ICP) instrumentation and operating conditions are described elsewhere (6). The elements, their wavelengths, and figures of merit are summarized in Table I. The IR spectra were recorded with a Perkin-Elmer 1320 IR spectrophotometer.

Reagents. Solutions were prepared from high-purity metals or ACS reagent grade chemicals. Distilled, deionized water was used throughout. Poly(ethylenimine) (PEI), MW 1800 (Polysciences, Warrington, PA), and polmeric isocyanate PAPI 135 (Upjohn Co., La Porte, TX) were used for the resin synthesis.

Resin Synthesis. *Method 1.* The polyamine–polyurea resin was prepared with a PEI/PAPI ratio of 8:1 as described by Hackett and Siggia (3). Subsequently the resin was reacted with carbon disulfide in ammonium hydroxide solution.

Method 2. After the preparation of the polyamine–polyurea resin described in method 1, pyridine was substituted for ammonium hydroxide during the reaction of carbon disulfide.

Procedure. *Thiocyanate Determination.* Fifty milligrams of resin was reacted at room temperature for 4 h in 10 mL of 1 N H_2SO_4. The resin was filtered and washed with distilled water. The filtrate was collected, and 2 mL of saturated bromine water was added, followed by 10 mL of concentrated formic acid. The solution stood for 10 min to allow the formic acid to react with excess bromine. Solid potassium iodide (50 mg) was added, and the solution stood for 20 min in the dark. The iodide was titrated with 0.02 N sodium thiosulfate. The determination is based upon the following reaction scheme (7):

$$SCN^- + 4Br_2 + 4H_2O \rightleftharpoons BrCN + SO_4^{2-} + 7Br^- + 8H^+$$

$$BrCN + 2I^- \rightleftharpoons I_2 + Br^- + CN^- \quad E = MW\ SCN/2$$

Metal Capacity Measurement of the Poly(dithiocarbamate) Resin. To 50.0 mg of resin (50–80 mesh), 20 mL of 1000 µg/mL

Table II. Elemental Analysis of Poly(dithiocarbamate) Resins

resin sample[a]	total,[b] mM N/g	total,[b] mM S/g	mM S/g (SCN)
1	13.0	6.50	2.07
2	13.5	6.09	1.70
3	12.2	3.43	0.98
4	12.3	3.86	0.53
5	12.2	3.30	0.16

[a] In order of decreasing red Fe(III) thiocyanate complex intensity. [b] By microanalysis.

Table III. Elemental Analysis of Resin 1 after Methanol Wash

	mM N/g	total mM S/g	mM S/g (SCN)
original resin	13.0	6.50	2.07
after methanol wash	12.0	4.88	1.02
difference	1.0		1.05

Cu, Co, or Fe(III) solution was added. The pH of the solution was adjusted to 4.6–4.8 with 2 M ammonium acetate. For Fe(III) the pH was 3.84. The resin was left overnight and then filtered through filter paper or a membrane filter. The resin was washed with distilled water to remove excess metals. The resin was ashed in an Erlenmeyer flask with 30% H_2O_2 at about 200 °C on a hot plate and digested with concentrated HNO_3 (8). Nitric acid was evaporated, and 0.6 mL of (1 + 1) HNO_3 was added to the residue. The final solution was diluted to 50 mL with distilled water.

RESULTS AND DISCUSSION

Ammonium hydroxide and carbon disulfide react forming thiocyanate (9), and the same reaction was presumed to occur during the preparation of the poly(dithiocarbamate) resin from the polyamine–polyurea resin when ammonium hydroxide was used (method 1). When pyridine was substituted as the base instead of ammonium hydroxide (method 2), thiocyanate cannot be formed. Based upon the infrared spectra of the poly(dithiocarbamate) resins synthesized by both methods, the resin prepared by method 1 contained thiocyanate groups as indicated by the strong absorption band at 2040 cm⁻¹. This absorption is absent in the IR spectrum of the resin that was prepared in pyridine. The determination of the thiocyanate content of both resins confirmed the IR spectra. The resin prepared in the presence of ammonium hydroxide contained 0.98 mM S/g measured as SCN, while the resin prepared in the presence of pyridine contained only 0.0078 mM S/g as SCN.

The analyses of poly(dithiocarbamate) resins that previously gave different intensities of the red coloration with Fe(III) solution are summarized in Table II. Total S content was determined by microanalysis. Resin 1 showed the deepest color with Fe(III) solution corresponding to the highest thiocyanate content. After preparation the resin was washed with methanol to remove labile thiocyanate. Resin 1 was washed with a large volume of methanol and analyzed again. Loss of nitrogen and sulfur (Table III) demonstrates that 1.0 mM SCN/g was removed by washing. Apparently, some of the thiocyanate is absorbed on the resin and can be washed away.

The role of the thiocyanate on the resin was evaluated by measuring the Cu, Co, and Fe resin capacity with different thiocyanate content. For the metals investigated, Cu(II) reacts with thiocyanate forming Cu(I) thiocyanate, which is a white precipitate, Co forms a CoSCN⁺ complex that is soluble, and Fe(III) forms red thiocyanato complexes, which are also soluble. These reactions were followed qualitatively during the capacity measurements. The Cu(I) thiocyanate precipi-

Table IV. Metal Capacities^a (mM/g) for Poly(dithiocarbamate) Resins with Different SCN Content

resin sample	mg S/g (SCN)	Cu	Co	Fe(III)
1	2.07	0.38	0.009	none
2	1.70	0.41	0.014	none
3	0.98	0.68	0.069	0.001
4	0.53	0.77	0.073	0.002
5	0.16	0.85	0.088	0.0043

^{a} Mean of triplicates. Relative standard deviations are 1.5–2.5%.

tation was observed when Cu(II) solution was added to the resin. Because in the capacity measurements the resin is filtered then ashed, the copper capacity refers to copper attached to the dithiocarbamate groups on the resin plus copper reacted with the thiocyanate groups on the resin forming the Cu(I) thiocyanate precipitate. The precipitate is filtered with the resin, but since the precipitate is somewhat soluble, the results can be ambiguous. The capacity measurements are summarized in Table IV.

The comparison of the Cu, Co, and Fe(III) resin capacity demonstrates that the higher the thiocyanate content of the resin the lower the capacity for the metal. Presence of thiocyanate groups on the resin is very unfavorable for the binding of the above elements. All metals that form thiocyanato complexes, e.g., most of the heavy metals, probably can react with the thiocyanate groups on the resin. Therefore, the metal uptake of the resin can be influenced by this reaction.

In conclusion, the poly(dithiocarbamate) resin should be prepared in the presence of pyridine instead of ammonium hydroxide so that only dithiocarbamate functional groups are formed on the polymer.

Registry No. SCN$^-$, 302-04-5; Cu, 7440-50-8; Co, 7440-48-4; Fe, 7439-89-6.

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Solution Phase Complexing of Atrazine by Fulvic Acid: A Batch Ultrafiltration Technique

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A batch ultrafiltration method for measuring atrazine complexing in fulvic acid solutions has been investigated experimentally. The method produces a dilution curve by using a set of dilutions of an atrazine stock solution. It has been demonstrated experimentally that this batch dilution curve method may be used for three purposes. The first purpose was to make direct diagnostic checks for ultrafiltration membrane interferences and other experimental errors. If any ultrafiltration membrane interferences exist, they were undetected above the level of the random analytical chemical errors in the cases tested. The other two purposes that have been met were to investigate the theory of methods for determining complexing capacity and complexing equilibrium and then to demonstrate them with experimental data.

The phenomena to be examined during research on reversible labile complexing of organic pesticides in fulvic acid

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solutions may include the complexing capacity of the dissolved fulvic acid and equilibria at loading below site saturation. It is convenient to have experimental methods that yield information about both phenomema together. In such solution phase investigations, the first and most general analytical chemical difficulty is the problem of measuring separately the free and complexed forms of at least one reactant. For some types of samples, spectrometric and electrochemical methods are not available. This is especially true of fulvic acid solutions, in which organic pesticides or metal ions are complexed. At least a few authors have reported the use of ultrafiltration methods for investigations of metal ion interactions with humic materials (*1–3*). Buffle and Staub (*4*) and Staub et al. (*5*) have published an experimental study of the batch dilution curve method for metal ions, together with a theoretical analysis of partial membrane permeability to fulvic acid. Almost concurrently, Haniff et al. have applied the batch dilution curve method to an investigation of the solution phase complexing of atrazine by fulvic acid (*6*). The work of several authors has made it clear that the risk of membrane interferences must be heeded (*7–10*). These requirements suggest the objectives of this work. One objective is to devise and