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D. J. Ehntholt^a; K. Thrun^a; C. Eppig^a; P. Ringhand^b

^a Arthur D. Little, Inc., Cambridge, Massachusetts, U.S.A. ^b Health Effects Research Laboratory, United States Environmental Protection Agency, Cincinnati, Ohio, U.S.A.

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The Concentration of Model Organic Compounds Present in Water at Parts-per-Billion Levels using Supercritical Fluid Carbon Dioxide†

D. J. EHNTHOLT, K. THRUN and C. EPPIG

Arthur D. Little, Inc., 15 Acorn Park, Cambridge, Massachusetts 02140, U.S.A.

and

P. RINGHAND

Health Effects Research Laboratory, United States Environmental Protection Agency, Cincinnati, Ohio 45267, U.S.A.

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Although hundreds of organic compounds have been identified in samples of natural waters, substantial amounts of the organic matter present cannot readily be characterized using current analytical techniques. Without such prior identification of the substances, they cannot be purchased or synthesized for use in the preparation of the concentrated solutions required for conducting health effects research.

We are conducting an evaluation of the use of supercritical fluid carbon dioxide to isolate and concentrate trace-level organics from aqueous samples. The use of carbon dioxide to effect concentration avoids the introduction of organic solvents or contaminants associated with other methods which may interfere with subsequent biological tests. Twenty-three organic substances have been chosen as representative of classes of compounds usually encountered in aqueous systems. We discuss herein the initial results obtained when aqueous solutions of fifteen of those organic compounds were extracted. The organics were added to water at parts-per-billion concentration levels; some inorganic salts were also added to the solutions to mimic natural waters. The technique has been demonstrated to work for most of the organics studied.

KEY WORDS: Concentration, organics, trace levels, supercritical fluid carbon dioxide.

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INTRODUCTION

One approach to understanding and evaluating the possible toxicological effects of the consumption of organic substances found in drinking waters is through the use of biological tests. Many of these tests challenge experimental animals or organisms and require concentration levels of the organic compounds which are significantly higher than normally found in drinking waters. Although hundreds of organic compounds have been identified and quantified in samples of natural waters, much of the organic matter present cannot readily be characterized using currently available analytical protocols. Without such prior qualitative and quantitative identification of the substances, they cannot be purchased or synthesized for use in preparation of the concentrated solutions required for health-effects testing.

Direct concentration of the organic materials from aqueous samples offers an attractive alternative which circumvents the analytical problems associated with the identification and quantification of wide varieties of species present at trace levels. A number of techniques have been studied for their utility in effecting such concentrations. These have included the use of reverse osmosis, solid sorbents, and liquid/liquid extracts.¹ Serious problems may, however, be encountered in the use of concentrated solutions prepared by these methods due to the inadvertant contamination of the sample. For example, membrane techniques may introduce impurities from the membrane, and may not selectively isolate organic substances from inorganic species. Collection of organics on sorbents followed by recovery with organic solvents also poses a number of problems. Concerns have been expressed over the large blank contributions of resins, possible interactions of the organic substances concentrated with the solvents (or impurities present in them) used for desorption, and the presence of traces of solvent in the prepared sample. The liquid/liquid extraction techniques utilizing organic solvents yield concentrations of organic substances in media which may be undesirable for animal feeding studies. For example, immediate concern can be expressed about the use of benzene or the halogenated one- and two-carbon compounds which are known or suspect carcinogens if long-term biological tests are to be performed.

We are conducting a study of the use of supercritical fluid carbon dioxide for the concentration and/or isolation of specified organic compounds present in waters at trace levels. This type of direct extraction using a non-toxic, non-hazardous solvent such as carbon dioxide represents an entirely new concept for extracting trace levels of organic compounds from water.

BACKGROUND

Solubility phenomena in supercritical fluids were first reported by Hannay and Hogarth in 1879.² They found that inorganic salts such as cobalt chloride and potassium iodide could be dissolved in supercritical ethanol and ether, and they found, furthermore, that the solubility level increased with increasing pressure.

In the early 1900's Bücher³ studied the solubilities of a number of organic materials in supercritical carbon dioxide. His studies focused on the determination of solution critical temperatures using low volatility compounds such as naphthalene, phenanthrene, phenols, and other aromatics. His results showed that the concentration of organic species dissolved in this supercritical solution was many times that which would be expected from the normal increase in vapor pressure due to external pressure (Poynting's correction). Other supercritical fluid solubility studies of the early 1900 period were directed to similar considerations of solution thermodynamics, multi-phase equilibria, solution critical loci, etc; Booth and Bidwell⁴ present an excellent review of the developments during this period.

During the 1940's, a large amount of solubility data was obtained by Francis^{5,6} who carried out measurements on literally hundreds of binary and ternary systems with liquid carbon dioxide just below its critical point. Francis found that liquid carbon dioxide is also an excellent solvent for organic materials and that many of the compounds studied were completely miscible.

Figure 1 gives some recent data which quantitatively shows the effect of pressure on the solubility of two organic materials in supercritical fluids, viz., *p*-iodochlorobenzene dissolved in ethylene⁷ and naphthalene dissolved in carbon dioxide.⁸ The figure shows that at low pressure, the pressure reaches some "threshold" value and the solubility subsequently increases rapidly. This threshold pressure in both cases is seen to be near the critical pressure, P_c , of the respective fluids. The threshold pressure above which solubility increases rapidly is, to some extent, a function of the system temperature, and at higher temperatures it may be higher than the critical pressure of the fluid as is seen in the naphthalene-ethylene solubility data of Diepen and Scheffer.⁹ As an example of the enhanced solubility of the two compounds, the respective solubilities calculated from vapor pressure considerations alone are shown in Figure 1, as a cross for *p*-iodochlorobenzene at 100 atm, and as a circle for naphthalene at 200 atm.

In 1955, Todd and Elgin¹⁰ reported on phase equilibrium studies with supercritical ethylene and a number of low vapor pressure organic

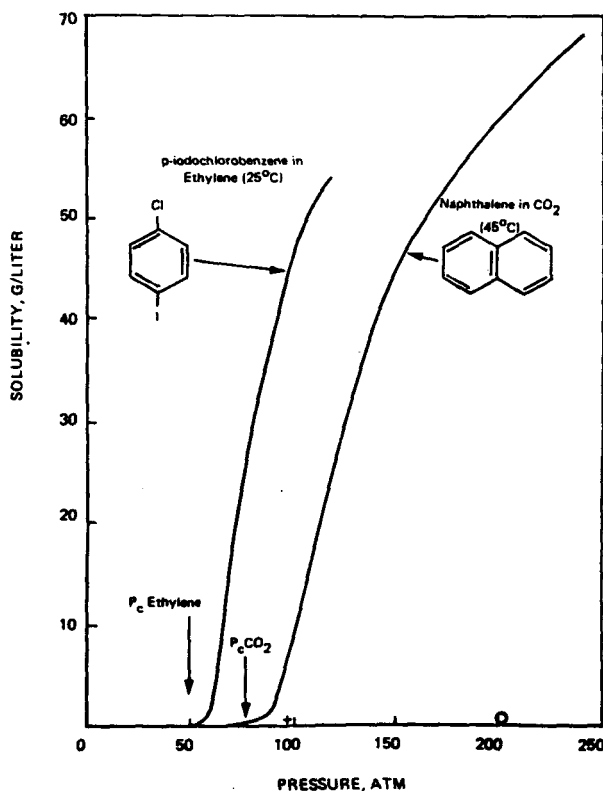


FIGURE 1 Solubility of organics in supercritical fluids.

materials such as fatty acids and high molecular weight alcohols, and like the investigators before them, they found solubility levels of the organic species to be orders of magnitude higher than those predicted by vapor pressure considerations. Their findings led them to write, "The magnitude . . . of solubility . . . is sufficient to consider the gas as an extracting medium, that is, fluid liquid or fluid solid extraction, analogous to liquid/liquid extraction and leaching . . . thus, compression of a gas over a mixture of compounds could selectively dissolve one compound, permitting it to be removed from the mixture." This was the first published reference to potential extraction process applications of solubility in supercritical fluids. A few years later Elgin and Weinstock¹¹ reported that a number of organic-water mixtures could be separated into organic-rich and water-rich phases using supercritical ethylene, and they presented process concepts for separating such mixtures. Since Todd and Elgin's paper in

1955, descriptions of a number of process applications of supercritical fluid solubility have appeared in the literature. Much of the effort reported has been directed to the extraction of edible¹² and essential¹³ oils and other food and beverage products such as spices,¹⁴ coffee,¹⁵ and hops¹⁶ using either supercritical or near-critical liquid carbon dioxide. The attributes of carbon dioxide, such as its low cost and absence of safety hazards and toxicity problems, were ideally suited for food applications. In the mid- to late-1960s some development activity was directed towards supercritical fluid chromatography¹⁷ and to extractions of fuels, viz., supercritical fluid extraction of coal,¹⁸ petroleum¹⁹ and lignite.²⁰

Starting in about 1975, development efforts at a number of industrial and academic laboratories increased markedly in both the United States and Europe. The resurgent research activity was motivated by a number of factors, viz.:

Increased scrutiny of certain industrial solvents because of associated health and safety problems,

Increasing costs of traditional but energy-intensive separation processes such as distillation and evaporation,

Increasingly stringent pollution control legislation which increased costs of traditional extraction processes,

Identification of certain key areas where supercritical fluid processing could be technically, as well as economically, superior to traditional separation processes.

Supercritical fluid separation processes operate at pressures ranging from 1,000 to 4,000 psi, a pressure which might be considered high, especially in the foods and essential oils industries. However, because of the above factors, supercritical fluid extraction is becoming economically attractive irrespective of the pressure requirements. Efforts to date have resulted in the development of several supercritical fluid processes in use throughout the world. Several large pilot plants for coal,²¹ coal ash,²² and asphalt²³ separation are in operation in the U.S., U.K., and U.S.S.R. Two commercial plants came on stream in 1979 for the extraction of beverage products, one in operation in Germany and the other in Australia, the former for coffee decaffeination²⁴ and the latter for hops extraction.²⁵ Theoretical and practical efforts leading to several of these developments were summarized at a recent symposium devoted to "Extraction With Supercritical Gases".²⁴

The development of new process applications of Supercritical Fluid technology has been an on-going activity at Arthur D. Little, Inc. since 1975. Work conducted there suggested the process advantages for

extracting low concentrations of organics from water, and these efforts were initiated in late 1980. This paper describes some of the initial results obtained in the program.

EXPERIMENTAL

Twenty-three organic substances were chosen as being representative of the various types of compounds which might be present in drinking water supplies. Those compounds and the concentration levels at which they are being investigated in this program are shown in Table I. The aqueous solutions for evaluation were prepared by spiking a small aliquot of the organic compounds dissolved in acetone into a distilled, deionized water

TABLE I
Organic substances selected for study

Group	Compound	Concentration level ($\mu\text{G/L}$)
1	1-Chlorododecane	5
	2,2',5,5'-Tetrachlorobiphenyl	5
	Biphenyl	50
	Bis(2-ethylhexyl)phthalate	50
	2,4'-Dichlorobiphenyl	50
2	Crotonaldehyde	50
	Furfural	50
	Isophorone	50
	Methyl isobutyl ketone	50
3	Anthraquinone	50
	Quinoline	50
	Caffeine	50
4	2,4-Dichlorophenol	50
	2,6-Di-t-butyl-4-methylphenol	50
5	Quinaldic acid	50
	Trimesic acid	50
	Stearic acid	50
6	Glucose	50
	Glycine	50
7	Chloroform	50
8	Phenanthrene	1
9	5-Chlorouracil	50
10	Humic acid	2,000

sample containing 70 ppm NaHCO_3 , 120 ppm CaSO_4 , and 47 ppm $\text{CaCl}_2 \cdot \text{H}_2\text{O}$.

Analytical methods for monitoring the compounds have been developed for all twenty-three materials. They are initially being studied by groups as designated in Table I. This approach assures minimal interferences in the analyses conducted during the supercritical fluid carbon dioxide extractions. Table II identifies the analytical techniques developed to monitor the concentration levels of the compounds before and after extraction by CO_2 .

Special care must be exercised in the study of parts-per-billion concentrations of organics in water to assure minimal losses due to sample degradation, adsorption or absorption to process materials, and other similar losses. In addition, in order to accurately determine the

TABLE II
Analytical methods for compounds under study

Group	Compound	Analytical method
1	1-Chlorododecane 2, 2', 5, 5'-Tetrachlorobiphenyl Biphenyl Bis(2-ethylhexyl)phthalate 2, 4'-Dichlorobiphenyl	GC/FID
2	Crotonaldehyde Furfural Isophorone Methyl isobutyl ketone	2, 4-Dinitrophenyl hydrazone derivatization, then HPLC/UV
3	Anthraquinone Quinoline Caffeine	GC/FID
4	2, 4-Dichlorophenol 2, 6-Di-t-butyl-4-methylphenol	GC/FID
5	Quinaldic acid Trimesic acid Stearic acid	Diazomethane derivatization, then GC/FID
6	Glucose Glycine	TMS/Oxime derivatization then GC/FID
7	Chloroform	GC/ECD
8	Phenanthrene	HPLC/UV/Fluorescence
9	5-Chlorouracil	HPLC/UV
10	Humic acid	HPLC/UV

levels of compounds present in the aqueous solutions before and after CO₂ extraction, prior concentration of many of the samples was necessary. In the case of Groups 1, 2, 3, 4, and 8, microextraction techniques with organic solvents were used.²⁶ For Group 5 acids, resin concentration is being used. Groups 6 and 9 are concentrated by evaporation; Group 7 (chloroform) and Group 10 (humic acids) can be analyzed as received. Derivatization is used to enhance the detection limits for three of the groups. The formation of 2,4-dinitrophenyl hydrazone derivatives of the Group 2 aldehydes and ketones permits their determination by an HPLC method after microextraction. Methyl esters of the Group 5 acids are formed using diazomethane, with subsequent detection by GC/FID. Glucose and glycine (Group 6) are quantified after treatment with a hydroxylamine hydrochloride solution in pyridine, followed by N-trimethylsilylimidazole. The TMS·glucose-oxime derivative and the glycine·TMS derivative thus formed can readily be analyzed using a GC/FID method.

In our work to date, the extractor has been operated at about 2,500 psi (i.e., 173 bar) and 45°C. (Supercritical conditions are achieved for carbon dioxide at pressures > 1,070 psi (i.e., 73.8 bar) and temperatures > 31.1°C). In our tests, approximately 300 standard liters of CO₂ were passed through the aqueous solution into the trap. The trapping system has consisted of a set of three sequential U-tubes maintained at -76°C. Operation at this temperature precludes clogging by solid CO₂, but may be responsible for loss of some extracted organic materials, as noted later. Laboratory scale carbon dioxide extractions have been conducted on 400 milliliter aliquots of the samples prepared as described above. To date, studies have been conducted on aqueous samples containing Groups 1, 2, 3, 4, and 10. The results obtained from supercritical fluid carbon dioxide extraction of dilute aqueous solutions containing these fifteen materials are discussed below.

APPARATUS

The experimental apparatus used to perform the supercritical fluid carbon dioxide extractions is shown diagrammatically in Figure 2. Carbon dioxide provided from supply cylinder 1 is compressed by diaphragm compressor 2 and heated to the desired extraction temperature in heat exchanger 3. The pressurized, temperature-adjusted carbon dioxide feed flows through the high pressure fluid inlet line 4 to vessel 6 which contains the aqueous solution to be extracted. The extraction vessel is wrapped with electrical heating tape to regulate the extraction temperature, which is measured with thermocouple 7.

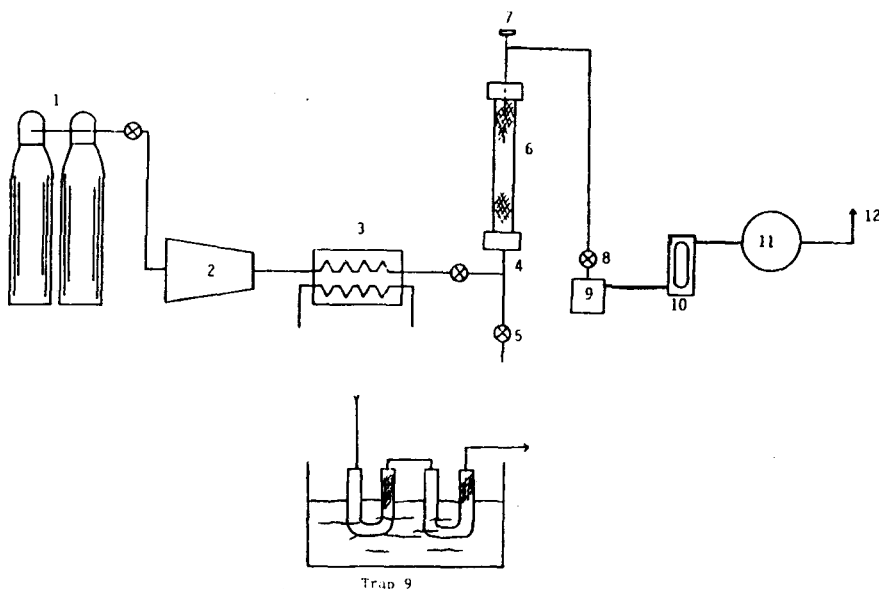


FIGURE 2 Supercritical fluid extraction apparatus.

The supercritical carbon dioxide extract stream is passed from the extractor vessel outlet through pressure reduction valve 8, where the pressure is reduced to atmospheric and the extracted organic substance is precipitated in collection device 9. The atmospheric pressure carbon dioxide then flows from the collection device through a rotameter 10 and dry gas meter 11, which measure CO_2 flow rate and total volume, respectively, to the vent 12.

To enhance the CO_2 /aqueous phase interfacial area and facilitate contact by dispersion of the CO_2 as fine bubbles, a plug of silanized glass wool is placed in the bottom of the extraction vessel. After charging the vessel with 400 mL of aqueous feedstock solution, the vessel is slowly pressurized to the extraction pressure and simultaneously heated to the desired temperature. Carbon dioxide is then passed through the aqueous phase at a superficial velocity of slightly more than 10 cm/min (about 10 standard liters/min at 1 atm., 70°F). After the desired amount of carbon dioxide has flowed through the sample, the system is depressurized and the extracted aqueous raffinate is drained through valve 5 into a collection vessel.

RESULTS AND DISCUSSION

Table III details the experimental results obtained for the supercritical carbon dioxide extraction of the Group 1 compounds. The compounds investigated, nominal spiking levels, and number of experiments performed are listed in the first three columns. The mean recoveries for each of the three U-tube traps connected in series are then presented along with the total recoveries obtained from all three traps. The quantity of compound recovered from the raffinate solution after CO₂ extraction is contained in the last column. Although four of the five compounds spiked into the aqueous samples could be recovered from the traps, only 20% to 31% of the total mass of each compound could be accounted for when the amounts in the traps and raffinate were summed. Losses may be due to incomplete trapping because of the relatively high vapor pressures of these compounds and the large volume of CO₂ passed through the traps. Table IV shows recoveries for the Group 2 aldehydes and ketones investigated. Results from the two experiments conducted on the aldehydes and ketones are shown separately to illustrate the care which must be exercised in conducting and evaluating these runs. Both CO₂ extractions were performed under similar conditions, however, in the second run the U-tube traps were contacted with the 2,4-dinitrophenylhydrazine derivatizing solution for significantly longer periods of time. This modification in the analytical procedure permitted higher total mass accountabilities in the second experiment, ranging from 64.9% for isophorone to 28.7% for methyl isobutyl ketone.

Table V details the extraction results found for Group 3 compounds anthraquinone, caffeine, and quinoline. The low trap recoveries and high residual concentrations of quinoline and caffeine in the raffinate solution suggest that the low pH of the extracting media (pH~3) reduces the solubility of these nitrogenous compounds in the CO₂ effluent stream. Anthraquinone was recovered in good yields from the same extractions.

Table VI presents our data for the similar extraction of Group 4 phenols from aqueous solutions. The *o*-bromophenol was added as an internal standard and is also reported here. The three phenols show good recoveries in the traps and overall good mass recoveries. One experiment was conducted under liquid CO₂ extraction conditions (temperature = 30°C and pressure = 1,500 psi) in an attempt to compare the relative efficiencies of the two states of CO₂ for phenol extraction. Unfortunately in this case, the phenols showed evidence of substantial "breakthrough" from the trapping system. The experiment does, however, demonstrate that liquid CO₂ is also a good extractant for phenols present in water at parts-per-billion concentration levels.

TABLE III
Group 1 extractions

Compound	Concentration level ($\mu\text{G/L}$)	Number of experiments	Trap recoveries (%)									
			Trap 1		Trap 2		Trap 3		Total traps		Raffinate	
			Mean recovery	Std. dev.	Mean recovery	Std. dev.	Mean recovery	Std. dev.	Mean recovery	Std. dev.	Mean recovery	Std. dev.
1-Chlorododecane	5	1	0	—	0	—	0	—	0	—	20.7	—
2,2',5',5'-Tetrachloro biphenyl	5	3	18.7	18.0	0	—	0	—	18.7	18.0	12.0	20.8
Biphenyl	50	1	9.1	—	11.0	—	3.3	—	23.4	—	3.8	—
Bis(2-ethylhexyl)phthalate	50	3	11.3	3.6	0	—	0	—	11.3	3.6	15.4	17.5
2,4'-Dichlorobiphenyl	50	3	15.7	2.6	4.6	—	0	—	20.3	2.6	8.5	10.8

TABLE IV
Group 2 extractions

Compound	Concentration level ($\mu\text{G/L}$)	Number of experiments	Trap recoveries (%)				Raffinate recovery
			Trap 1 recovery	Trap 2 recovery	Trap 3 recovery	Total Traps recovery	
Crotonaldehyde	50	2	0.8	0	0.2	1.0	25.1
			7.0	0.8	0	7.8	31.0
Furfural	50	2	3.7	0	0.1	3.8	43.4
			8.3	2.5	0	10.8	22.3
Isophorone	50	2	0	0	1.7	1.7	17.8
			39.2	0.7	0.5	40.4	24.5
Methyl isobutyl ketone	50	2	0	0	0	0	7.4
			15.6	1.5	0.2	17.3	11.4

TABLE V
Group 3 extractions

Compound	Concentration level ($\mu\text{G/L}$)	Number of experiments	Trap recoveries (%)									
			Trap 1		Trap 2		Trap 3		Total traps		Raffinate	
			Mean recovery	Std. dev.	Mean recovery	Std. dev.	Mean recovery	Std. dev.	Mean recovery	Std. dev.	Mean recovery	Std. dev.
Quinine	50	2	1.7	1.7	1.7	1.7	0	3.4	3.7	46.1	14.3	
Caffeine	50	2	0	0	0	0	0	0	—	81.4	11.4	
Anthraquinone	50	2	56.0	14.3	14.3	14.3	84.6	38.3	21.4	30.2	30.2	

TABLE VI
Group 4 extractions

Compound	Concentration level ($\mu\text{G/L}$)	Number of experiments	Total recoveries (%)						
			Trap 1	Trap 2	Trap 3	Total traps		Raffinate	
			Mean recovery	Mean recovery	Mean recovery	Mean recovery	Std. dev.	Mean recovery	Std. dev.
2,4-Dichlorophenol	50	3(SCF CO ₂)	35.8	9.6	0	45.4	15.0	28.0	14.0
		1(Liquid CO ₂)	15.3	16.8	8.2	40.3	—	13.4	—
2,6-Di- <i>t</i> -butyl-4-methylphenol	50	3(SCF CO ₂)	26.6	6.0	0	32.7	3.0	0	—
		1(Liquid CO ₂)	8.7	10.7	6.6	26.0	—	6.8	—
<i>o</i> -Bromophenol	50	3(SCF CO ₂)	24.6	17.0	0	41.7	15.6	31.6	9.6
		1(Liquid CO ₂)	10.8	12.3	10.8	33.9	—	19.5	—

Several extractions have also been conducted on 2.0 milligram/liter humic acid solutions. These were prepared by dissolving a known quantity of humic acid (Fluka) in 0.20 M sodium hydroxide followed by dilution with water to a 0.02 M sodium hydroxide solution. Subsequent neutralization to pH 7.0 with 0.100 M HCl and dilution with water containing the salts noted earlier gave a 2.0 mg/L humic acid solution for extraction studies. Three supercritical fluid carbon dioxide extractions were carried out on this solution; no humic acid could be detected in the traps.

Table VII lists extraction conditions tried in these runs. It was also observed that although the analyses of feedstock solutions showed the presence of 97.7% to 104.7% of the expected concentration levels of humic acids, analyses of raffinate solutions showed lower humic acid concentrations. The raffinate obtained after the CO₂ extraction indicated that the humic acids were present at 39.4% to 44.9% of the feedstock levels. This suggests that the acidic conditions present in the extractor caused some acid precipitation and resultant loss of material.

TABLE VII
Extraction conditions for 2.0 ppm humic acid solutions

Experiment No. 1:	Charge:	400 mL of solution
	Temperature:	45°C (± 3°)
	Pressure:	2,400 psi (± 100)
	CO ₂ Volume:	300 standard liters
Experiment No. 2:	Charge:	400 mL
	Temperature:	46°C (± 3°)
	Pressure:	2,450 psi (± 50)
	CO ₂ Volume:	340 SL
Experiment No. 3:	Charge:	400 mL
	Temperature:	46°C (± 3°)
	Pressure:	2,200 psi (± 50)
	CO ₂ Volume:	580 SL

Since it has also been of interest to demonstrate whether or not salts can be carried over and concentrated by this extraction technique, we have examined the trapping system after "blank" runs. In those cases, solutions containing only the specified levels of salts (i.e., NaHCO₃, CaSO₄ and CaCl₂) were extracted by supercritical fluid CO₂. The results are presented in Table VIII, and show that the sodium and calcium salts were not carried into the trapping system.

TABLE VIII
Extraction of aqueous salt solutions

Analyte	Sodium analysis ^a (mg)	Calcium analysis ^b (mg)
Distilled water		
Total traps	0.15	0.03
Raffinate	<0.2	0.03
Solution No. 1		
Total traps	0.08	0.06
Raffinate	8.0	15.2
Solution No. 2		
Total traps	0.03	0.01
Raffinate	8.0	16.0
Solution No. 3		
Total traps	0.11	0.04
Raffinate	8.8	16.0

^aTotal sodium expected in solutions = 7.7 mg.

^bTotal calcium expected in solutions = 18.2 mg.

These results summarize our efforts to date. Extractions are planned for solutions containing the other compounds listed in Table I in the near future. Calculations which we have made pursuant to the use of our current trapping system suggest that we may be experiencing some loss of the organics due to their finite vapor pressures in the -76°C effluent CO_2 stream. We are therefore examining modifications to the system which will minimize such losses. In addition, we anticipate scaling up our process to demonstrate the extraction of 500 liters of an aqueous solution containing all of the compounds of interest. It should be possible to process this volume within a twenty-four hour period, thus minimizing adsorption losses, bacterial changes or other phenomena which might influence the sample's integrity.

It is our expectation that this novel process will find application in the rapid processing of large volumes of aqueous solutions. It has utility from the standpoint of collection and concentration of organics from water but can also be viewed as a treatment technology to remove selected chemicals from aqueous effluent streams.

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References

1. Several recent reviews describe these efforts, for example:
 - a. F. W. Karasek, R. E. Clement and J. A. Sweetman, *Analytical Chemistry* **53** (9), 1050A (1981).
 - b. R. L. Jolley, *Environmental Science and Technology* **15** (8), 874 (1981).
2. J. B. Hannay and H. Hogarth, *J. Proc. Roy. Soc. (London)* **29**, 324 (1879).
3. E. H. Buchner, *Z. Physik. Chem.* **54**, 665 (1906).
4. H. S. Booth and R. M. Bidwell, *Chem. Rev.* **44**, 447 (1949).
5. A. W. Francis, *J. Phys. Chem.* **58**, 1099 (1954).
6. A. W. Francis, *Liquid-Liquid Equilibriums*, Interscience Publishers, John Wiley and Sons (1963).
7. A. H. Ewald, *Trans. Faraday Society* **49**, 1401 (1953).
8. Yu. V. Tsekhanskaya, M. B. Iomtev and E. V. Mushkina, *Zh. Fiz. Khim.* **38**, 2166 (1964).
9. G. A. M. Diepen and F. E. C. Scheffer, *J. Phys. Chem.* **57**, 575 (1953).
10. D. B. Todd and J. C. Elgin, *AIChE Jour.* **1**, 20 (1955).
11. J. C. Elgin and J. H. Weinstock, *J. Chem. Eng. Data* **4** (1), 3 (1959).
12. Br. Pat. 1,356,749.
13. L. G. Aleksandrov, S. A. Popova and V. I. Serdyuk, *Tr. Krasnodar. Nauchno-Issled. Inst. Pishch. Promitr.* **6**, 146 (1973).
14. Br. Pat. 1,336,511.
15. Br. Pat. 1,346,134.
16. Br. Pat. 1,388,581.
17. J. C. Giddings, M. N. Myers and J. W. King, *J. Chromatog. Sci.* **7**, 276 (1969).
18. K. O. Bartle, T. G. Martin and D. F. Williams, *Fuel* **54**, 226 (1975).
19. C. A. Irani and E. W. Funk, "Separations Using Supercritical Gases" in *Recent Developments in Separation Science*, N. Li, Ed., CRC Press, Cleveland.
20. T. Tugrul and A. Olcay, *Fuel* **57**, 415 (1978).
21. R. R. Maddocks and Gibson, Jr., *Chem. Eng. Progr.* **59**, (1977).
22. R. M. Adams, A. H. Knebel and D. E. Rhodes, *Chem. Eng. Prog.* p. 44 (1979).
23. P. F. M. Paul and W. S. Wise, *The Principles of Gas Extraction*, Mills and Boon, London (1971).
24. G. M. Schneider, E. Stahl and G. Wilke (Eds.), *Extraction With Supercritical Gases*, Verlag Chemie, Weinheim, West Germany (1980).
25. F. V. Harold and B. J. Clark, *The Brewers Digest*, p. 45, September 1979.
26. K. E. Thrun, K. E. Simmons and J. E. Oberholtzer, *J. Environ. Sci. Health* **A15**, (5), 485 (1980).