NWRI CONTRIBUTION 88-102

SUPERCRITICAL FLUID EXTRACTION OF 2,3,7,8 TETRACHLORO DIBENZO-P-DIOXIN FROM SEDIMENT SAMPLES

by

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NWRI Contribution Number 85-113

November 1988

MANAGEMENT PERSPECTIVE

This study reports the use of various supercritical fluids for the extraction of 2,3,7,8-TCDD from spiked Hamilton Harbour sediments.

The two primary determinants of extraction efficiency are shown to be the solubility of 2,3,7,8-TCDD in a supercritical fluid and the water content in the sediment. Extraction with the nitrous oxide + 2% methanol showed that rapid and almost complete recovery of 2,3,7,8-TCDD is possible. The presence of water slowed the extraction of 2,3,7,8-TCDD from the sediment.

Current work is seeking to optimize an energetic regime of the extraction based on the enthropy-temperature and pressure data for 2,3,7,8-TCDD in a particular supercritical fluid.

Dr. J. Lawrence
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PERSPECTIVE DE GESTION

Cette étude fait état d'une expérience d'utilisation de divers fluides supercritiques pour l'extraction du 2,3,7,8-TCDD de sédiments enrichis prélevés dans le port de Hamilton.

Les deux principaux déterminants de l'efficacité de l'extraction se sont révélés être la solubilité de 2,3,7,8-TCDD dans un fluide supercritique ainsi que la teneur en eau des sédiments. L'extraction effectuée à l'aide d'oxyde d'azote + 2 % de méthanol a montré que l'on pouvait récupérer rapidement et presque complètement 2,3,7,8-TCDD. La présence d'eau a ralenti l'extraction de ce composé dans les sédiments.

Les travaux en cours cherchent à optimiser le régime énergétique d'extraction à partir des données sur l'enthropie-température et sur la pression pour 2,3,7,8-TCDD dans un fluide supercritique particulier.

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ABSTRACT

Supercritical fluid extraction (SFE) of 2,3,7,8 tetrachloro dibenzo-dioxin (2,3,7,8-TCDD) from contaminated sediments is a promising technique for its removal from environmental matrices. The ability of SFE to solubilize many organic contaminants is well documented in industrial processes but its analytical applications were exploited just recently. In this study, supercritical carbon dioxide and nitrous oxide and their mixtures with 2% methanol were used to extract 2,3,7,8-TCDD from aquatic sediments. An attractive feature of this process is that the carbon dioxide, being a virtually inert fluid, leaves no solvent residue on the processed sediment. Almost 100% of the 2,3,7,8-TCDD can be extracted from a sediment spiked with 200 μg/kg 2,3,7,8-TCDD in 30 minutes by using supercriticial carbon dioxide plus 2% methanol. Cleanup procedure is compared with the Soxhlet extraction procedure currently used as a standard method for extracting dioxins from sediment samples.

RÉSUMÉ

L'extraction dans un fluide supercritique de 2,3,7,8 tétrachlorodibenzo-dioxine (2,3,7,8-TCDD) dans des sédiments contaminés semble être une méthode prometteuse pour l'extraction de ce composé dans les matrices environnementales. La capacité de cette méthode à solubiliser de nombreux contaminants organiques est bien connue pour les procédés industriels, mais ses applications pour l'analyse ne sont exploitées que depuis peu de temps. Dans cette étude, du gaz carbonique supercritique et de l'oxyde d'azote ainsi que leur mélange dans 2 % de méthanol ont été utilisés pour extraire 2,3,7,8-TCDD contenu dans des sédiments aquatiques. Caractéristique intéressante de cette méthode : le gaz carbonique, qui est pratiquement un fluide inerte, ne laisse aucun résidu de solvant sur le sédiment traité. Près de 100 % de 2,3,7,8-TCDD peuvent être extraits d'un sédiment enrichi avec 200 ug/kg 2,3,7,8-TCDD en 30 minutes à l'aide d'un mélange de gaz carbonique supercritique plus 2 % de méthanol. La méthode de nettoyage est comparée à la méthode d'extraction Soxhlet couramment utilisée comme méthode standard pour extraire les dioxines des échantillons de sédiments.

1.0 INTRODUCTION

The extraction of a component from a solid matrix with a liquid ranks with distillation as one of the most useful separation techniques. Most of the modern food, pharmaceutical, cosmetic and oil industries have their origin in liquid-solid extraction processes to concentrate naturally occurring components into more concentrated products. The extraction processes in many technological areas are known under different names such as leaching, washing, percolation and elution. At one time, the term solvent extraction referred only to extraction of a solid. However, with the development of liquid-liquid extraction on a large scale under the same title, a less ambiguous name is desirable. Until recently, the use of supercritical carbon dioxide extraction (SFE) has been generally related to large-scale chemical processing applications for coal (1), asphalt (2), coffee decaffeination (3), hops extraction (4) and fractionation of polymeric materials (5).

In the beginning of the 1980's, the emergence of supercritical fluid chromatography (6) and supercritical fluid extraction (7) as viable analytical techniques have generated considerable interests in many areas of organic analytical chemistry. It is one of the most significant new techniques in analytical chemistry and new applications are being developed frequently. Supercritical fluid extraction is a separation technique based on the enhanced solvating power of supercritical fluids above their critical point. Supercritical fluids are compressed gases at a temperature just above their vapor-liquid critical point, and have unique physical properties that can be used to develop novel selective separation procedures. Supercritical fluid extraction has the ability to selectively extract many compounds that are thermally labile and it is claimed (8) that it will be suitable to extract high molecular weight components from a matrix, such as sediment, fish tissues, biota and fauna without the use of a liquid extraction. The solubility of organic solutes in supercritical fluids

is often many times greater than the solubility in a gaseous phase. Density changes of the supercritical phase (extractant) are principal factors in achieving high solubility and separation selectivity. The ratio of these solubilities is called the enhancement factor, which is defined as the ratio of actual solubility in supercritical fluid to ideal gas solubility (9). Thermodynamic treatment of the multiphase equilibria has been discussed in detail (9).

Since there is a definite relationship between temperature and supercritical fluid density, the role of temperature in regulating solvating power is obvious. Similarily, pressure changes at constant temperature can affect a dense gas's solvating characteristics. Thus, by regulating both, temperature and pressure, highly selective behaviour of supercritical fluids can be attained.

2.0 EXPERIMENTAL

2.1 Apparatus

In general, a supercritical extraction system consists of a high pressure pumping system, an extraction cartridge and a source of supercritical fluid. When the system operates in a closed-circuit mode and equilibrium is reached, the extraction is said to perform under steady-state conditions. However, microscale SFE-systems do not utilize steady state extraction but operate without reaching equilibrium.

The operation of such a system is straightforward. A sample to be extracted is placed into the sample holder and the extractor is pressurized to initiate the extraction process. A supercritical fluid is recycled by an in-line compressor and when equilibrium is reached depressurization of the extractor is initiated. The initial pressure in the extractor is reduced gradually and solute-vapor mixture is transferred to a separator. These extractors have certain advantages when compared to the non-steady state leaching systems. They may be used for obtaining essential chemical engineering data needed for modelling purposes (11).

We built a micro-SFE system, a diagram of which is shown in Fig. 1. This extractor is based on the non-steady state principle as described by Hawthorne et al. (12-14). In our system, there are some refinements which we consider essential for improvement of reproducibility of the extraction process. We have been using a 501 Model pump purchased from Lee Scientific Inc. (Salt Lake City, Utah, USA). The sediment sample is weighed into a 0.5 mL extraction cell constructed of a sintered stainless steel cup and stainless steel housing as shown in Fig. 2. Supercritical conditions are maintained inside the extraction cell by restricting the outlet flow with the use of a 25 to 30 μm I.D. and 15 cm long fused silica restrictor (HIRESCO, Mississauga, Ontario). A new restrictor is used for every second extraction. It has been observed that a single restrictor if used for several extractions yields lower recoveries due to changes in hydrodynamic profile caused by deposition of non-soluble particles and eventual plugging of the capillary.

The extract can be collected by inserting the restrictor into a collection vial, containing up to 5 mL of n-hexane spiked with an internal standard (d-12 pyrene, 0.2 μg/mL) or directly can be introduced on a pre-column of an open tubular column using GC/MS. If an extract is collected in n-hexane, the solvent is evaporated gently under stream of nitrogen to approximately 50 μL volume. Since sensitivity of an FID is not sufficient for majority of environmental samples and purity of SFC grade carbon dioxide is not guaranteed by the supplier (Scott Speciality Gases, Inc.), so that utilization of an electron capture detector is not practical, a selective ion monitoring GC-MS alternative is the only technique that can provide the required selectivity and sensitivity.

2.2 Sediment Samples

Wet sediment (approximately 500 g) taken from Hamilton Harbour was spread evenly in a shallow glass dish to air dry at room

temperature in a contaminant free area. The sample was stirred and mixed occasionally during drying to break it into small pieces. This process was continued until the sample appeared visually dry and free flowing. The dried sample was then manually ground to a fine powder with a mortar and pestle. The sediment contained 8% total organic carbon and 0.22% total organic nitrogen.

2.3 Apparatus - Soxhlet Extractor

The apparatus includes a 500 mL round-bottom flask, heating mantle with variable voltage control, Soxhlet extractor (100 mL capacity) and a Liebig water-cooled condenser.

2.4 Extraction of Sediments - Soxhlet Extraction Method

A 10 mm layer of solvent extracted Celite was placed in an extraction thimble. A 1.00 g of sediment was placed over the Celite. A 150 mL volume of n-hexane-acetone (1:1) plus 25 mL of 2,2,4-trimethylpentane and some boiling chips were added to the round-bottom flask. Extraction was carried out continuously for 18 hours. This time was selected experimentally because it provided 100% recovery. After cooling, the extract was transferred with 2 x 10 mL n-hexane rinsing to a 250 mL round flask and concentrated by rotoevaporation. The cleaned up fractions were gas chromatographed on SE-52 fused silica columns using helium as a carrier gas. The temperature program for the column oven was 60°C to 260°C at 4°C/min. All identifications were confirmed by HRGC-MS. The methods of analysis are described in greater detail (16) elsewhere.

2.5 Gas Chromatographic Analyses

All GC analyses were performed with a Carlo Erba 4160 gas chromatograph equipped with the on-column injector. We used thin film

0.17 μm, 30 m x 0.25 mm I.D. SE-52 crosslinked fused silica column. Extraction and cleanup for 2,3,7,8-TCDD was described in detail elsewhere (16, 17).

2.6 Gas Chromatography-Mass Spectrometry-Selected Ion Monitoring

Significant problems in quantitation of 2,3,7,8-TCDD was observed when very low concentrations of individual contaminants were analyzed using an electron capture detector. It was found that even supercritical carbon dioxide and nitrous oxide are not suitable for analysis because very large spurious peaks are present in these fluids. Using GC/MS, these peaks were identified as chlorofluoro hydrocarbons, that are used for cleaning pressurized cylinders. It should be noted that the manufacturer is claiming concentration lower than 10 ppt for freons. According to our data, we found concentrations more than 10,000 times higher. To eliminate the spurious peaks, selected ion monitoring is the best solution.

3.0 RESULTS AND DISCUSSION

The first sediment sample used to demonstrate the effectiveness of supercritical CO_2 (at 310 atm and 40°C) was spiked with 2,3,7,8-TCDD. Extractions of this spiked sediment showed that approximately 48% of the 2,3,7,8-TCDD could be removed in 30 minutes as shown in Figure 3. Longer time extractions did not show significant improvements. These data imply that a portion of 2,3,7,8-TCDD is strongly bound to the sediment and that supercritical carbon dioxide at these conditions cannot extract this stongly adsorbed 2,3,7,8-TCDD.

In order to study the effects of various supercritical fluids, we replaced carbon dioxide with nitrous oxide. Extraction data for a 2,3,7,8-TCDD spiked sediment (200 μg/kg) were obtained to compare to the previous results. These results are given in Figure 3. For the spiked toxicant, there was significant improvement in

extraction efficiency but again only 91% of the 2,3,7,8-TCDD was extracted with nitrous oxide in 30 minutes.

The extraction of the 2,3,7,8-TCDD contaminated sediment proved to be more effective when entrainers were added to the previous supercritical fluids. As is evident from the data in Figure 4 over 93% removal was achieved in under 30 minutes with supercritical CO_2 + 2% methanol and 100% extraction was achieved with supercritical N_2O at 40°C. Apparently, there were no appreciable rate limitations in this extraction.

The effect of sediment was content on the supercritical fluid CO_2 + 2% methanol extraction was investigated by extracting both dry and wet sediment. The sediment sample was prepared by centrifuging it for 10 minutes at 5000 rpm. The moisture content was about 20%. This sediment was spiked and then extracted under the usual conditions. The wet sediment was then extracted under the usual conditions. These results are given in Figure 5. When compared to the corresponding dry sediment, there was a slower rate of removal of the 2,3,7,8-TCDD. The final concentrtion of 2,3,7,8-TCDD in the sediments was comparable to those obtained from dry sediment extractions.

The rapid extraction of 2,3,7,8-TCDD by means of supercritical nitrous oxide with 2% methanol at 40°C and 310 atm contrasts sharply with extraction of supercritical carbon dioxide efficiency, under the same conditions. The most likely explanation focusses on the different polarity of carbon dioxide and nitrous oxide. As it can be seen from Figure 3 a dramatic increase in the extraction efficiency is obtained even for pure fluids as it was observed by Hawthorne et al. (14) and Laner et al. (18). An addition of methanol as an entrainer to both fluids noticeably improves the extraction of 2,3,7,8-TCDD from the sediment. Methanol increases solubility of 2,3,7,8-TCDD due to its specific interactions between the entrainer and the solute. Different entrainers in supercritical fluid extraction can be utilized to increase selective extraction based on their ability to form hydrogen bonds or Lewis acid-base interactions.

A careful choice of the supercritical fluid and entrainer permits the 2,3,7,8-TCDD to be extracted by an optimum solvent mixture.

In this preliminary study, we investigated also an effect of the moisture of the sediment on the kinetics of extraction and recovery. Results indicate that approximately 20% moisture decreases extraction efficiency as far as time required for achieving an equivalent enrichment. However, it is possible to obtain the same results but the time required for extraction must be doubled.

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FIGURE CAPTIONS

Figure 1. Schematics of the Supercritical Fluid Extraction System: 1) cylinder; 2) the pumping system; 3) collection of the extract; 4) extractor; 5) 6-way valve; 6) an oven; 7) preheating coil.

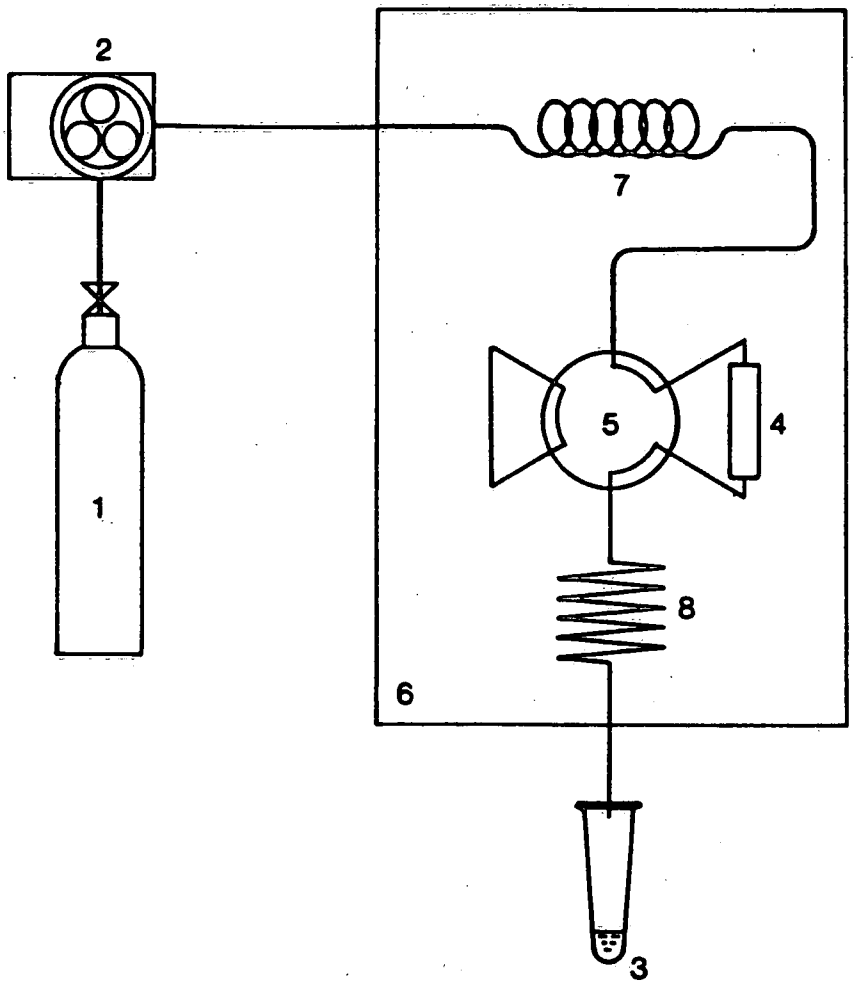
Figure 2. Supercritical Fluid Extractor: 1) capillary tubing; 2 and 7) nuts; 3) porous disc cover; 4) O-ring; 5) porous SS-cup; 6) cartridge; 8) fitting for the restrictor.

Figure 3. Extraction Efficiency of Carbon Dioxide and Nitrous Oxide for 2,3,7,8-TCDD from Sediment Samples.

Figure 4. Extraction Efficiency of Carbon Dioxide and Nitrous Oxide Containing 2% Methanol for 2,3,7,8-TCDD from Sediment Samples.

Figure 5. Effect of Water Content on the Extraction Efficiency of Carbon Dioxide + 2% Methanol for 2,3,7,8-TCDD from a) dry and b) wet sediment samples.
1 dry sediment; 0.3% (w/w) water
2 wet sediment; 19.8% (w/w) water. Extraction conditions as in Fig. 4.

Figure 6. Comparison of Extraction Efficiency of 2,3,7,8-TCDD using Different Fluids and Soxhlet Extraction.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7
1
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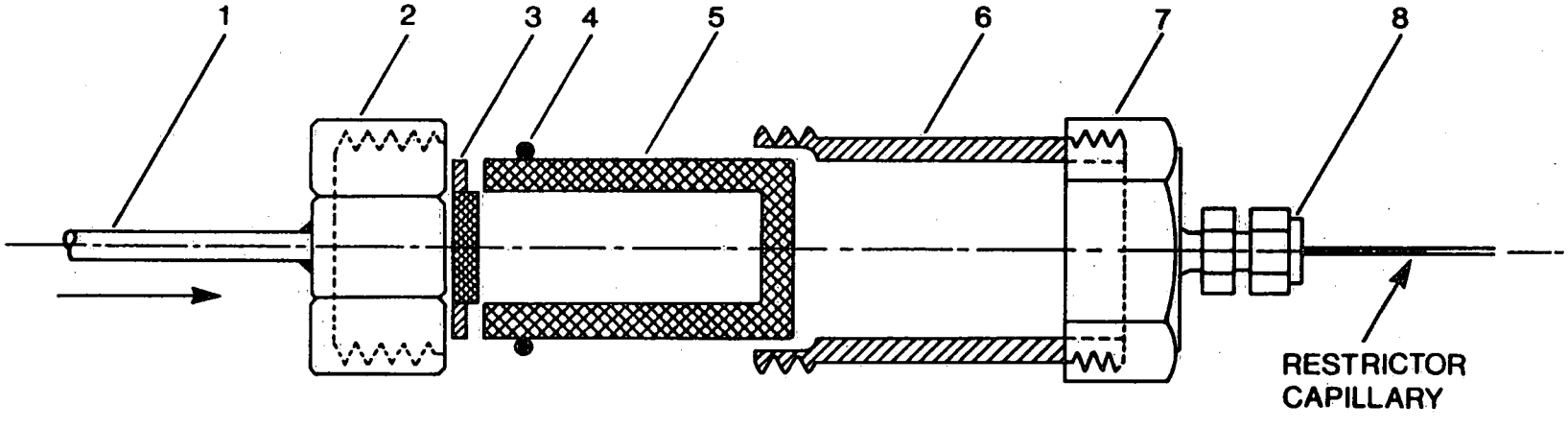
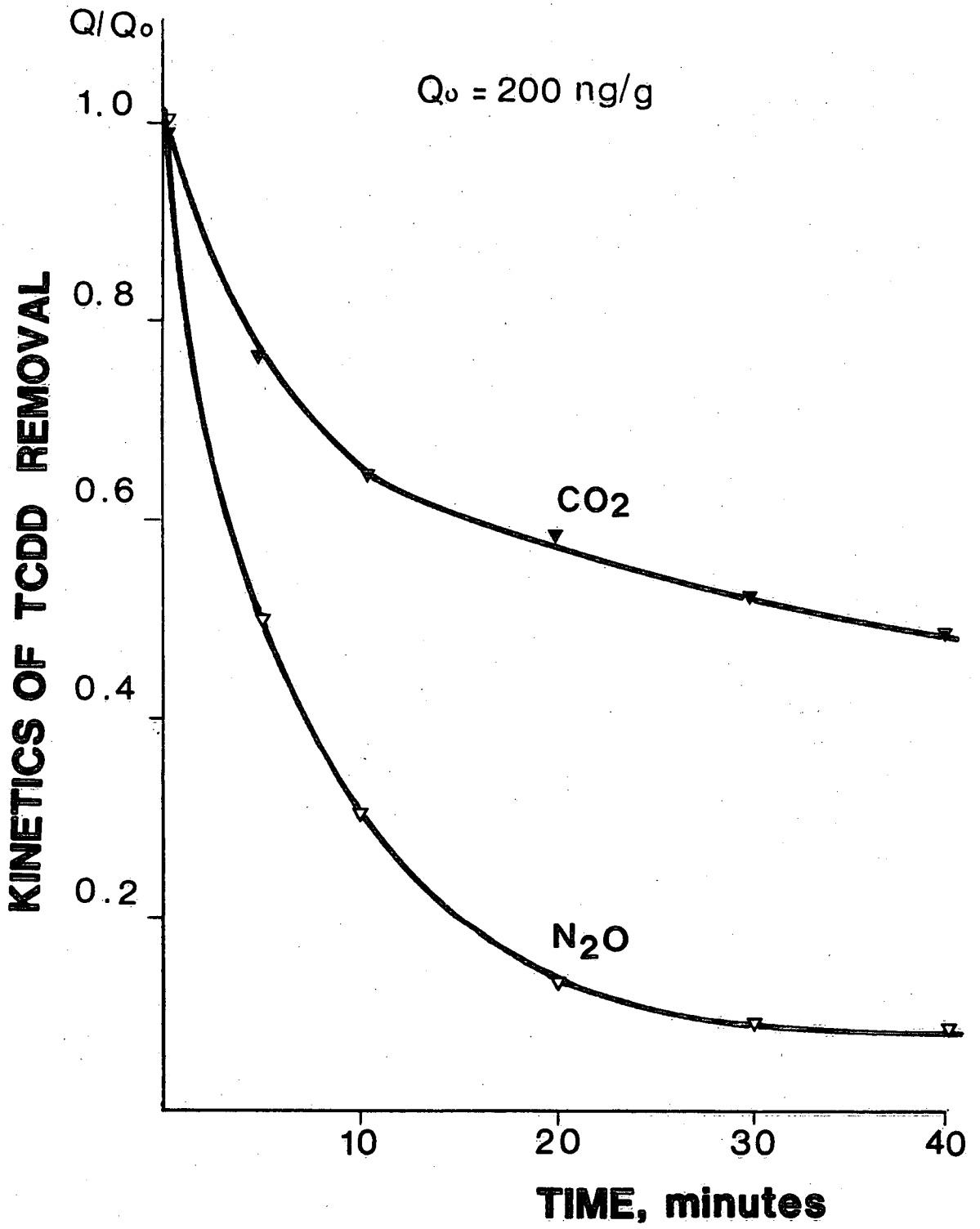
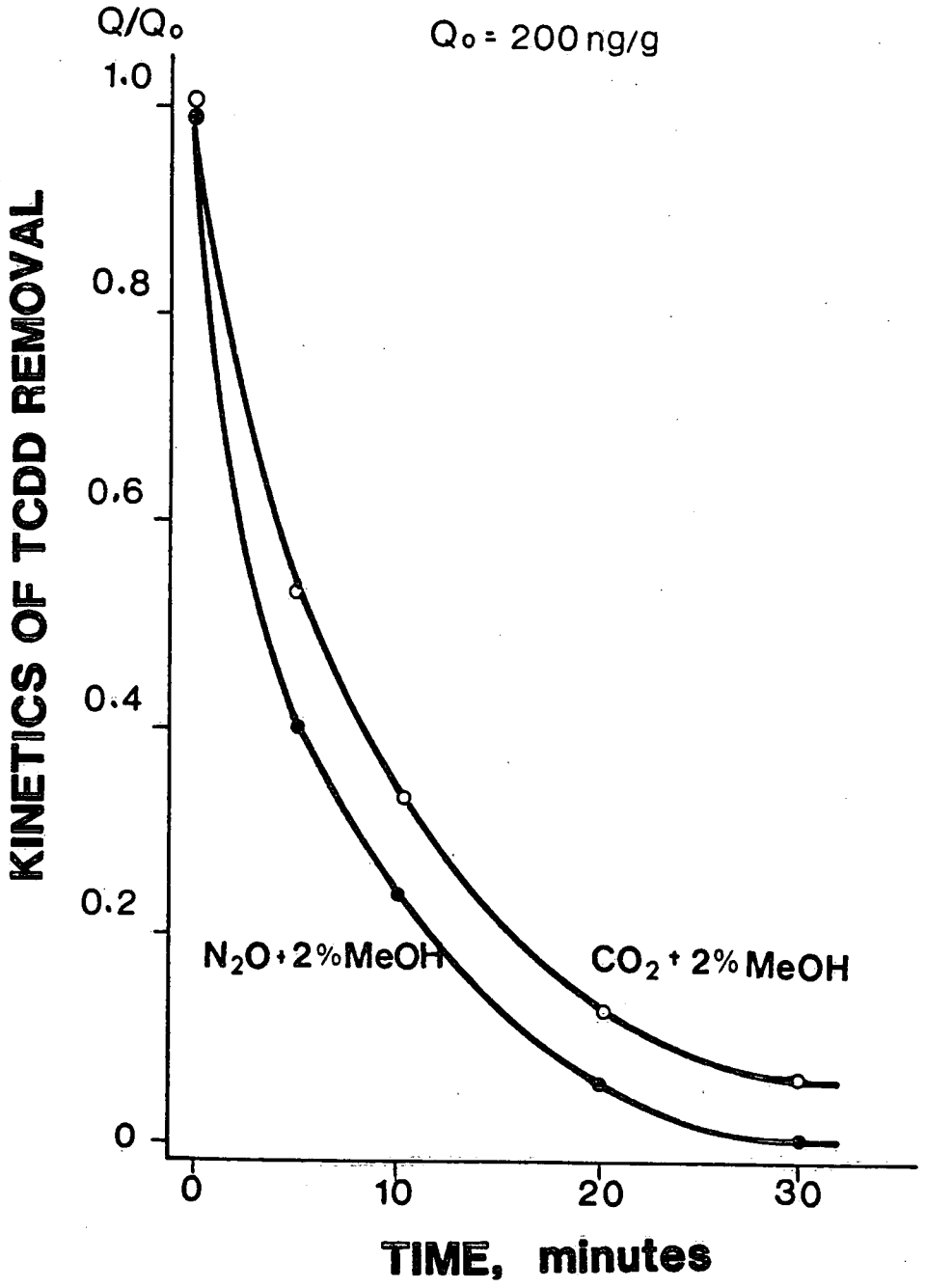
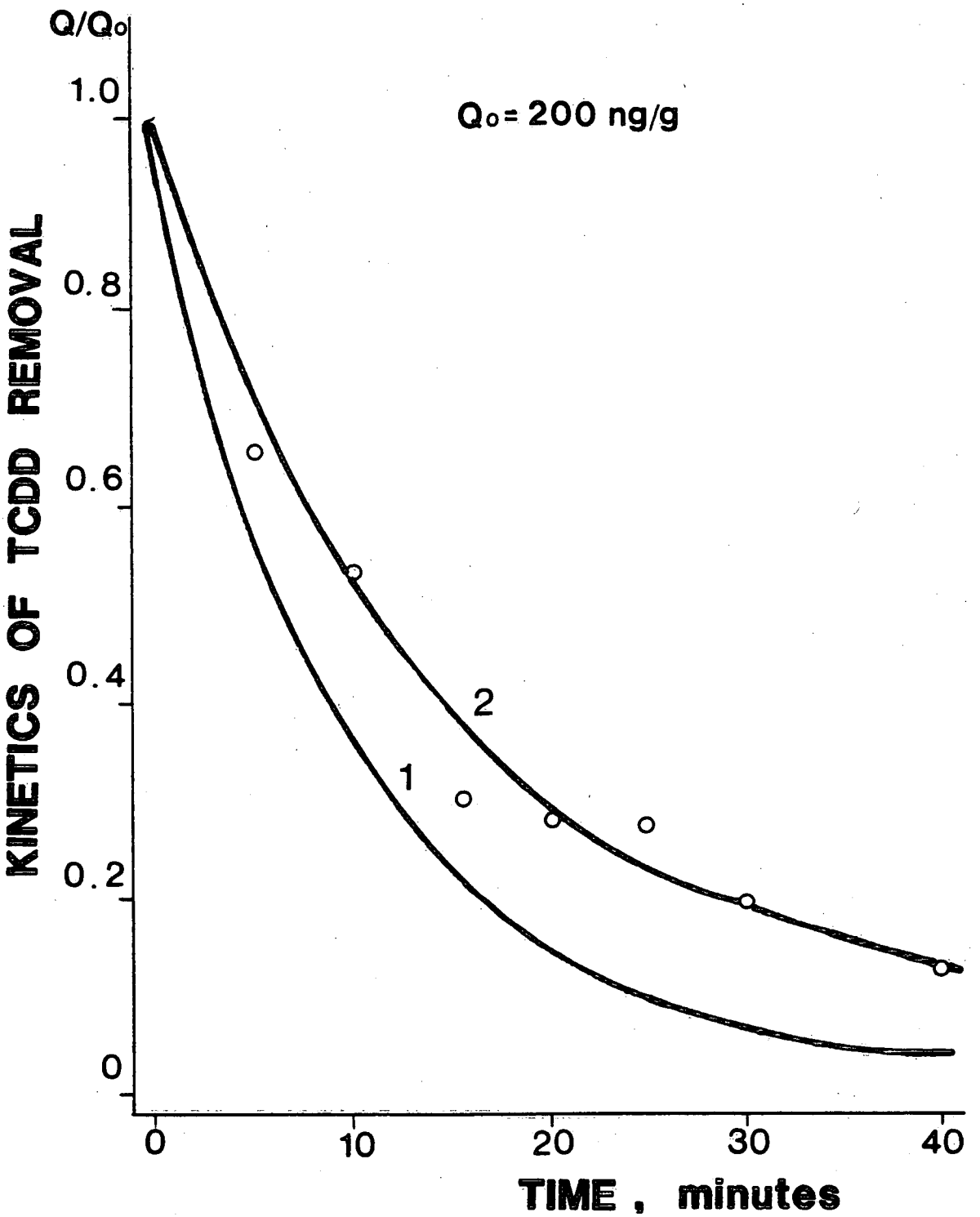
4
8
6
3



SF EXTRACTOR


Q/Q₀
1.0
0.8
0.6
0.4
0.2
Q₀ = 200 ng/g
CO2
N2O
KINETICS OF TCDD REMOVAL
10
20
30
40
TIME, minutes


Q/Q₀
Q₀ = 200 ng/g
1.0
0.8
0.6
0.4
0.2
0
KINETICS OF TCDD REMOVAL
N₂O + 2% MeOH
CO₂ + 2% MeOH
0
10
20
30
TIME, minutes


KINETICS OF TCDD REMOVAL
Q/Q₀
1.0
0.8
0.6
0.4
0.2
0
Q₀= 200 ng/g
1
2
0
10
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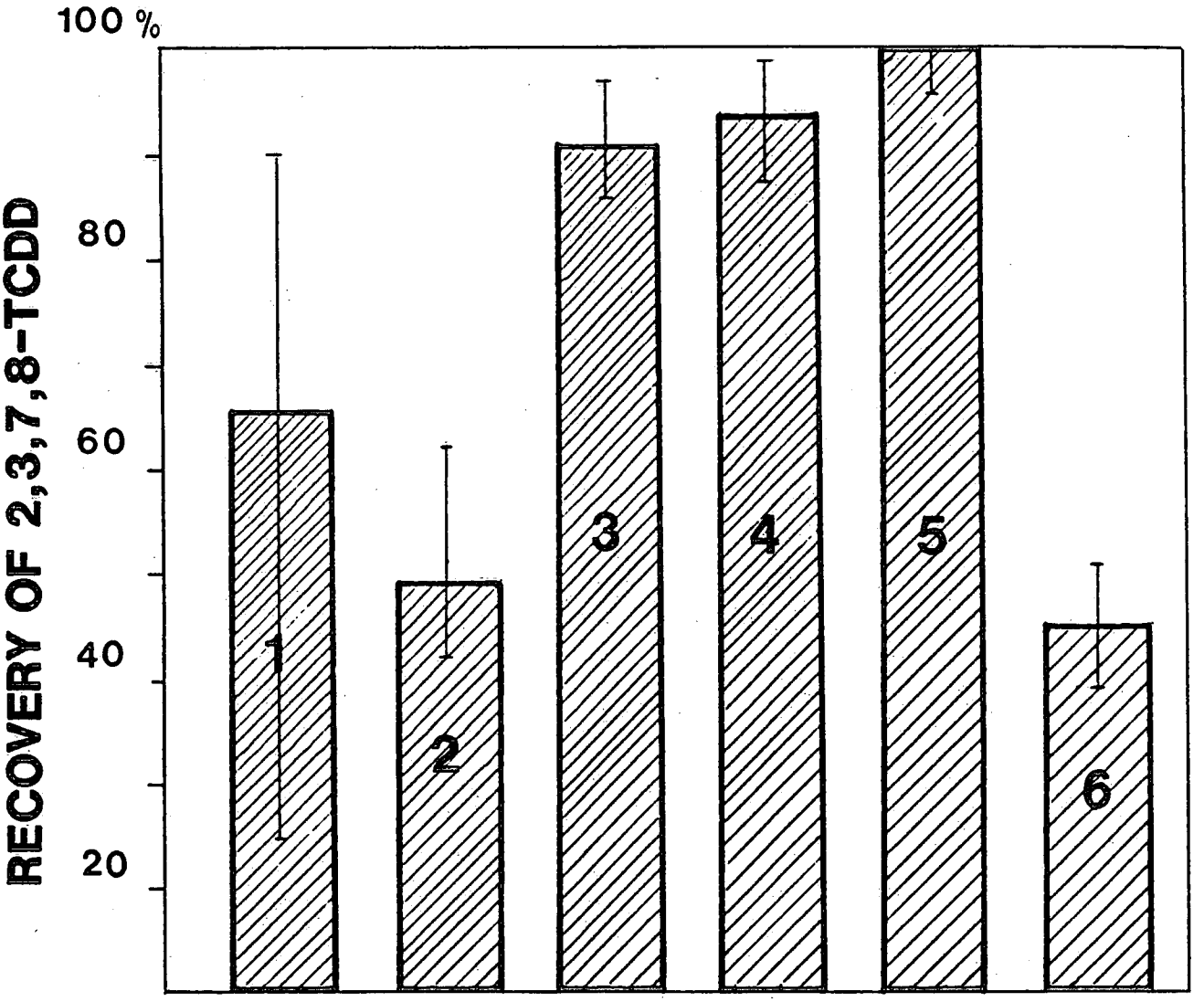
30
40
TIME , minutes



1 SOXHLET
2 Carbon dioxide
3 Nitrous oxide
4 Carbon dioxide - 2% methanol
5 Nitrous oxide - 2% methanol
6 Sulfur hexafluoride