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SUPERCRITICAL FLUID CHROMATOGRAPHY OF ALKYLENE OXIDE - FATTY ALCOHOL CONDENSATES: THEIR QUANTITATION IN WATER SAMPLES

by

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MANAGEMENT PERSPECTIVE

This manuscript reports supercritical fluid chromatography as a new technique suitable for separation and determination of non-volatile and thermally unstable compounds. Non-ionic surfactants were selected as model compounds. These detergents are often discharged into municipal and industrial waters causing severe environmental problems namely foam buildup in rivers and reservoirs. As a consequence, insufficient aeration occurs and it may result in oxygen depletion of the water.

The developed method allows selective isolation of non-ionic surfactants and their biodegradation products with high recoveries and precision. It is the first time that quantitative results using SFC in environmental analysis have been reported.

Dr. J. Lawrence
Director
Research and Applications Branch

PERSPECTIVES DE GESTION

Le présent document provisoire décrit la chromatographie à fluide supercritique comme nouvelle technique convenant à la séparation et à l'analyse de composés non volatils et thermiquement instables. Des agents tensio-actifs non ioniques ont été choisis comme composés modèles. Ces détergents sont souvents déversés dans les eaux municipales et industrielles avec, comme conséquence, de graves problèmes environnementaux, comme la formation de mousse dans les cours d'eau et les réservoirs. Il s'ensuit une aération insuffisante, qui peut provoquer une carence d'oxygène dans l'eau.

La méthode mise au point permet d'isoler sélectivement les agents tensio-actifs non ioniques, ainsi que leurs produits de biogradation, avec un taux de récupération et une précision très élevés. C'est la première fois que des résultats quantitatifs d'analyses environnementales par CFS sont ainsi présentés.

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RÉSUMÉ

Une méthode est décrite pour l'analyse quantitative de condensats d'oxydes d'alcoylène linéaires et d'alcools gras, agents tensio-actifs non ioniques dans l'eau. L'agent tensio-actif est extrait des échantillons d'eau à l'aide de benzène. Il est ensuite soumis à une extraction supplémentaire grâce au chloroforme. La chromatographie capillaire, à fluide supercritique, permet la séparation et l'analyse quantitative de constituants oligométriques, avec du dioxyde de carbone comme fluide supercritique. Dans ce cas, on arrive à une caractérisation de l'agent. Cependant, la durée de l'analyse est d'environ 60 minutes. Dans le second cas, les groupes éthers-oxydes des condensats d'oxyde d'éthylène et d'alcool gras sont scindés par réaction avec de l'acide bromhydrique 50 % dans de l'acide acétique glacial, en ampoules scellées. Les bromures d'alcoyle résultants sont soumis à une extraction au disulfure de carbone, et analysés à la fois par chromatographie à fluide supercritique, par chromatographie sur colonne capillaire en phase gazeuse, sur colonne tubulaire ouverte, haute résolution (CPGHR-CTO). Il y a une bonne corrélation entre les résultats des deux techniques.

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SUMMARY

A method is described for the quantitative determination of linear alkylene oxide - fatty alcohol condensates, nonionic surface active agents in water. Surface active agent is extracted from water samples with benzene. Surfactant is further extracted by salting out into chloroform. Capillary, supercritical fluid chromatography allows the separation and quantitative determination of oligometric constituents using carbon dioxide as a supercritical fluid. In this case, a fingerprint of the surfactant is obtained. Analysis time, however, is approximately 60 minutes. In the second case, the ether groups of ethylene oxide fatty alcohol condensates are cleaved by reaction with 50 percent hydrobromic acid in glacial acetic acid in sealed ampoules. The resulting alkyl bromides are extracted with carbon disulfide and chromatographed by both the supercritical fluid, capillary column chromatography (SFC) and high resolution open tubular column gas chromatography (OTC - HRGC). Results are in good agreement between these two techniques.

INTRODUCTION

Surface active agents and their technical mixtures are organic chemicals which change the interfacial properties of liquids. They are added as general purpose detergents and emulsifiers in agricultural and cosmetic formulations and softening agents for textile fibres. Surfactants are usually classified into four groups : nonionic, cationic, anionic and amphoteric. A total of about 50 million metric tons of cleaning agents are manufactured worldwide per year (1). Nonionic surfactants are the second most used surfactants after anionic types. These compounds do not possess either negative or

positive charges. The most important group of nonionic surfactants are reaction products between ethylene oxide and different organic residues such as fatty alcohols, alkyl phenols, polyhydric alcohols, fatty acid alkanolamines and glycerides.

Surface active agents are discharged into municipal and industrial waters causing several environmental problems namely foam build up in rivers and reservoirs. As a consequence, insufficient aeration occurs and it may result in oxygen depletion of the water and fish-kills.

The techniques most widely used for the determination of nonionic surfactants detect the parent surfactant material (2). They provide no information about nonionic surfactant biodegradability. On the other hand, metabolic methods (3,4) more closely approach the determination of the ultimate biodegradability by mineralization to carbon dioxide but are also non-informative of the nature of intermediate products.

As an example of the value of such an approach, we described in 1976 (5,6) biodegradation studies of a linear alcohol ethoxylate which exhibits rapid primary degradation and slower ultimate degradation of the polyethoxylene moieties. A gas chromatographic method and selective extraction techniques were employed to examine the intermediate products occurring during the biodegradation.

Supercritical fluid chromatography (SFC) has developed from the combination of supercritical fluid carbon dioxide as a mobile phase with narrow-bore open tubular columns and its

compatibility with the flame ionization and mass spectrometric detectors (6,7) and is advantageous in comparison with liquid chromatographic methods. One common feature of the high performance liquid chromatographic analysis of nonionic surfactants is the difficulty of their detection because with the exception of alkylphenol ethoxylates they do not absorb in the UV-region. In spite of the obvious potential, SFC has not yet gained general acceptance in environmental trace analyses.

A technique for the quantitation of alkylene oxide-fatty alcholol condensates using the packed column gas chromatography described previously (5) has been improved in this paper. The results of the HRGC and the SFC using narrow-bore capillary columns are presented below. Both techniques allow selective isolation of nonionic surfactants and of polyglycol biodegradaion products with high recoveries and sufficient precision offering a useful alternative to techniques previously used in nonionic surfactant biodegradation studies.

EXPERIMENTAL

Materials and Reagents. All solvents were nanograde quality and were used without further purification. n-Hexane and chloroform as well as carbon disulfide were purchased from Anachemia (Mississauga, Ont.), polyethylene glycol 400 was obtained from Chromatographic Specialtiies, Brockville, Ont. 1-Nonanol, 1-dodecanol, 1-tetradecanol and 1-hexanol were purchased as kit No. 124 from Poly Science Corp., Evanston, Ill., USA. Dobanol 25-9 was received from Shell Research Laboratories, Egham, Surrey, England. Average structure is n-$C_{12-15}H_{25-31}O(C_2H_4O)_9H$.

Extraction and Cleanup. The water samples were extracted according to the standard procedure for determining alkylene oxide-fatty alcohol condensates (5). To eliminate contaminants interfering in the extraction, samples were pretreated as recommended by Pitter and Baxantova (8). One litre of sample was mixed with 2.5 mL of 10 % $ZnSO_4.7H_2O$ solution and 2.5 mL of saturated $Ba(OH)_2$. After boiling and cooling, the sample was filtered through quantitative filter paper and extracted from 30 % $MgSO_4.7H_2O$ solutions (9) with four 20 mL portions of chloroform. The pooled chloroform extracts were evaporated on a Rotavap to a volume of 1 mL, then transferred quantitatively through glass wool and anhydrous $MgSO_4$ to a 1 mL ampoule. The internal standard, 1-nonanol, was added to the ampoule (1 mL of 200 mg/mL and 5 uL of 200 mg/mL in ethanol was used for Dobanol 25-9 concentrations of 4 and 800 ug/mL, respectively). Solvent was evaporated from the ampoule at 40 °C on a heating block.

Formation of n-Alkylbromides. After evaporation of solvent, the residue in each ampoule was reacted with 0.5 mL of HBr reagent (BDH Laboratory Reagents) as described earlier (5). The products were taken up in saturated aqueous bicarbonate solution and extracted into 2 mL CS_2. The carbon disulfide extract was transferred through 0.5 g glass wool into a Hypovial (Pierce Chem). An external reference mixture consisting of polyethylene glycol 400, 1-nonanol, 1-dodecanol, 1-tetradecanol and 1-hexadecanol was reacted simultaneously with each set of samples to allow external quantitation of the results. Aliquots of these extracts were then analyzed by SFC and HRGC.

Supercritical Fluid Chromatography (SFC). For the SFC analyses the SFC system consisted of the Lee Scientific pumping and injection systems and Dani, Model GC-oven with the IBM-XT personal computer and appropriate software purchased from the Lee Scientific Co., Salt Lake City, Utah, U.S.A. The injection technique used was a pneumatically driven, rotary microvalve. The inlet from the microvalve to the narrow-bore column was equipped with an adaptor for split injections, even though the rotary valve could be actuated rapidly without a splitter. However, a 50 um I.D. capillary column can be easily overloaded without the splitter and it is better to use a splitter.

The column was prepared by deactivating a 10 m x 50 um I.D. fused silica tubing (Polymicro Technology, Phoenix, AZ) with dimethoxydiphenylsilane using low temperature silanization (10) and by statically coating a 0.25 um film of PS 265 (Petrarch Chemical, Bristol, PA, U.S.A.) in n-pentane on the column wall and crosslinking with azo tert.-butane. Samples to be analyzed were introduced into the narrow-bore column with a 0.2 uL internal sample volume Valco valve in conjunction with an inlet splitter. Pressure restriction and connection to the flame ionization detector was accomplished by making an integral restrictor at the end of the column using a modified procedure of Guthrie and Schwartz (9). The oven temperature was held constant at 140 °C for CO_2 and the detector temperature was maintained at 280 °C.

High Resolution Gas Chromatography (HRGC) and HRGC/ Mass Spectrometry. The gas chromatographic analyses were performed using a Carlo Erba Model 4160 gas chromatograph equipped with a conventional flame ionization detector and a cool on-column injector. A 30 m x 250 um I.D. SE-52XL OTC (0.17 um film thickness) supplied by Hiresco (Mississauga, Ont., Canada) was used. The same OTC was used in Shimadzu QP-1000 GC/MS system for identification of retention products employing the same chromatographic conditions. The detailed description and analytical instrumentation and procedures for HRGC, HRGC/MS have been described previously (10).

RESULTS AND DISCUSSION

Supercritical Fluid Chromatography Separations.

Figure 1 shows narrow-bore SFC separation obtained by the analysis of alkylene oxide-fatty alcohol condensates. The complexity of the mixture is remarkable. The number of components containing oligomeric fatty alcohol polyethoxylates with 1 to 9 ethoxy units show multiple peaks. The total analysis time is approximately 60 minutes. Corresponding oligomers with the same number of ethoxy units but different fatty alcohol moieties show at least 80 different peaks. By variation of the density of carbon dioxide, it is possible to extend the range of oligomers that can be determined much beyond that illustrated by the given fingerprint of the surfactant. However, the quantitative analysis using the flame ionization detector is not satisfactory due to unknown composition of individual peaks and their responses. Preliminary evidence of HRGC analysis of the

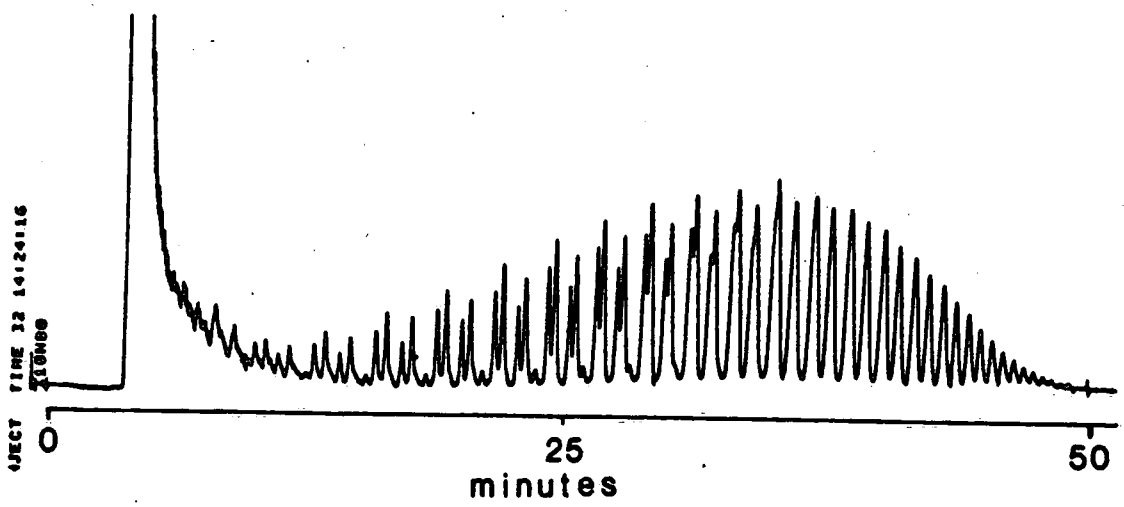

Figure 1. Supercritical Fluid Chromatogram of Dobanol 25-9 Surfactant.
Conditions : 9 m x 50 um I.D. FS-column SE-52XL(crosslinked), 0.3 um film thickness. Carbon dioxide mobile phase at 140 °C; density programmed from 0.25 g/mL to 0.65 g/mL @ 0.01 g/mL to 0.4 g/mL, 0.006 g/mL to 0.5 g/mL and 0.008 g/mL to 0.65 g/mL.

mixture provided did not give conclusive results either, (Figure 2) and for this reason, we concluded that this type of fingerprint is suitable only for the qualitative characterization of a particular surfactant. Due to the required amount of sample that must be injected as a 15 percent solution, it is not suitable for quantitation in environmental trace analyses.

The complexity of commercial linear alkylene oxide-fatty alcohol condensates was greatly simplified by the HBr/glacial acetic acid procedure (Figure 3 and 4). Peaks were identified by comparison of their retention times with standards and confirmed by HRGC/MS. The first peak in all chromatograms was identified as

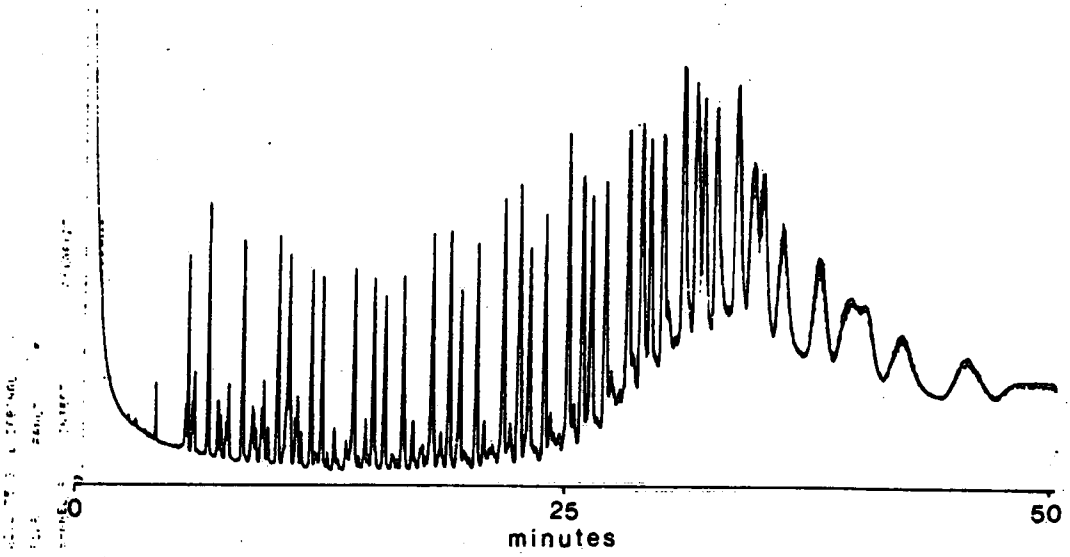

Figure 2. Gas Chromatogram of Dobanol 25-9 Surfactant. Conditions are given in text. Temperature programmed from 70 °C to 280 °C @ 5 °C/min and hold for 10 minutes.

1,2-dibromoethylene. Individual fatty alcohol moieties were converted to 1-bromododecane, 1-bromotridecane,1-bromotetradecane and 1-bromopentadecane. The normalization of peak areas allowed quantitation of a variety of fatty alcohols. In all cases the comparison of results obtained by HRGC and SFC using internal standardization with 1-nonanol was in good agreement. The number of peaks in both chromatograms was reduced significantly and standardization of individual peaks was very simple since pure alcohols were readily available.

Tables 1 and 2 illustrate the experimental results of replicate sample analyses. The apparent lower sensitivity by SFC is caused by the small amount of sample entering the FID. Only 0.2 uL of a sample was introduced onto our system and a split

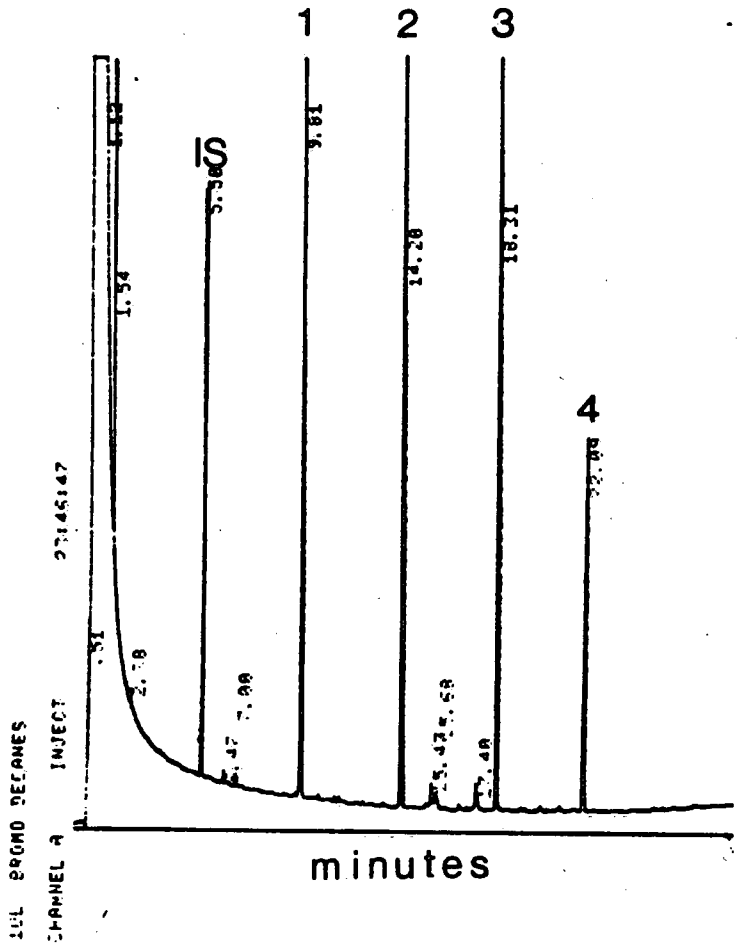

Figure 3. Gas Chromatogram of HBr Cleaved Dobanol 25-9. Conditions are described in footnotes under Table 1. Peak identification : IS 1-bromononane; 1 1-bromododecane; 2 1-bromotridecane; 3 1-bromotetradecane; 4 1-bromopentadecane.

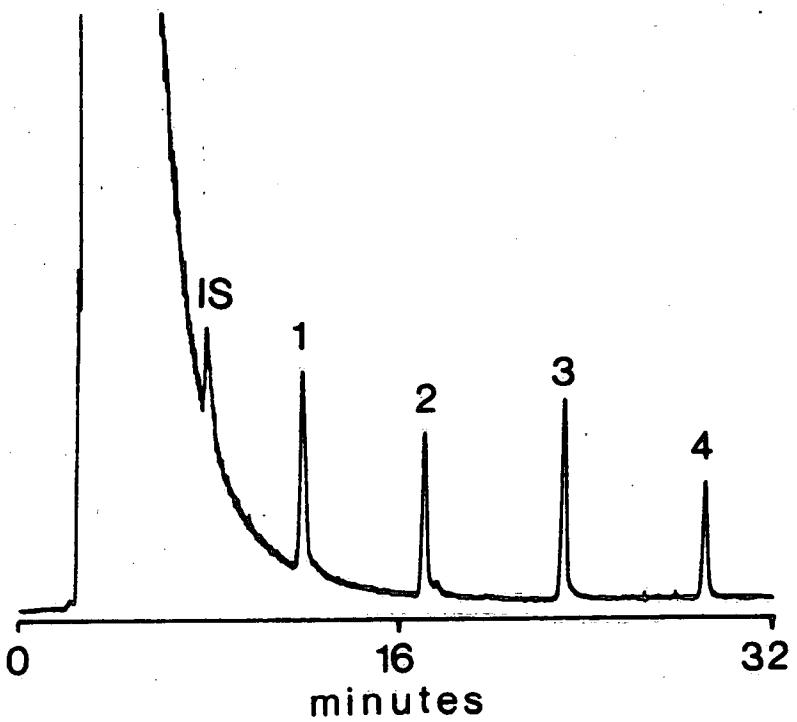

Figure 4. Supercritical Fluid Chromatogram of HBr Cleaved Dobanol 25-9.
Conditions are given in footnotes under Table 2.
Peak identification : IS 1-bromononane; 1 1-bromododecane, 2 1-bromotridecane; 3 1-bromotetradecane; 4 1-bromopentadecane.

Table 1. Dobanol Spike Recoveries by means of GC-FID at Two Levels.

Compound	C-12 Br		C-13 Br		C-14 Br		C-15 Br	
Level (ug/g)	4.00	800.0	4.00	800.0	4.00	800.0	4.00	800.0
1	3.36	752	3.16	696	3.20	720	3.24	728
2	3.24	728	3.24	728	3.16	712	3.24	728
3	4.04	808	4.12	824	4.08	816	4.12	800
4	3.92	792	3.84	776	3.88	784	3.88	784
5	3.48	776	3.48	776	3.28	792	3.36	752
6	4.00	800	4.00	800	3.96	736	4.04	808
Mean	3.673	776	3.64	766.7	3.593	760	3.647	766.7
S.D.	0.354	30.78	0.404	47.03	0.398	42.93	0.411	35.57
CV	0.096	0.039	0.110	0.061	0.110	0.057	0.112	0.046

HRGC conditions : 30m x 0.32mm I.D. SE-52XL, cool on-column injection at 70 °C programming to 240 °C at 6 °C/minute.

Table 2. Dobanol Spike Recoveries using Supercritical Fluid Chromatography at Two Levels.

Component	C-12 Br		C-13 Br		C-14 Br		C-15 Br	
Level (ug/g)	4.00	800	4.00	800	4.00	800	4.00	800
1	3.36	704	4.04	840	3.40	712	3.24	680
2	3.16	600	3.36	704	3.60	720	3.28	624
3	3.68	704	3.60	709	3.84	807	4.00	880
4	4.02	832	3.08	586	3.66	688	3.32	698
5	3.65	697	3.60	752	3.46	720	3.48	669
6	3.09	640	3.77	789	3.40	649	3.19	659
7	3.55	737	3.96	758	3.28	666	3.44	658
Mean	3.501	702	3.63	734	3.52	708.9	3.421	695.4
S.D.	0.324	73.49	0.335	80.19	0.190	51.23	0.275	84.49
CV	0.093	0.105	0.092	0.109	0.054	0.072	0.080	0.122

SFD Conditions : 9m x 50um I.D. SE-52XL OTC, d_f=0.3 um. Split injection 0.2 uL; 1 sec injection time duration.

SFC Program: Initial CO_2 density 0.12; ramp density 0.005/min; final density 0.27 for 30 minutes; oven temperatue 140 °C; detector temperature 280 °C.

ratio of approx. 1:50 was used. The injection technique in supercritical fluid chromatography represents the bottleneck in environmental quantitation of micropollutants and it has to be improved before the technique is applicable to environmental analysis. Since large quantities of nonionic surfactants are being introduced to the environment as domestic and industrial wastes as well as oil spill dispersants, the environmentally damagging effects of these chemicals, other than foaming problems are becoming apparent, making it essential that environmental impact studies of the nonionic surfactants be continued. Clearly, supercritical fluid chromatography has a bright future and it will be indispensable in the environmental laboratory for understanding biodegradation of many more pollutants. We are just starting to explore its potential and we believe that it will be another powerful analytical tool in the near future.

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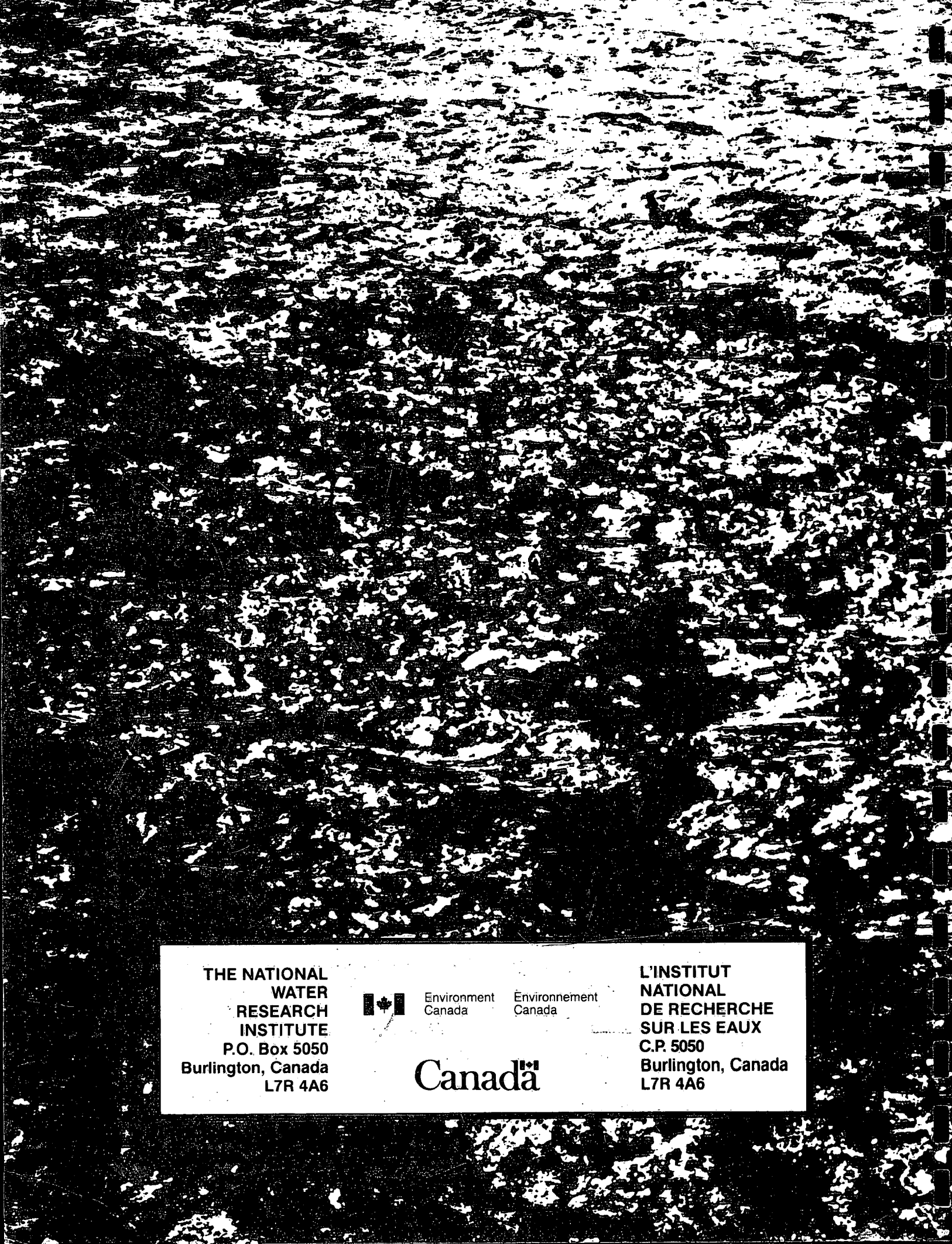

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