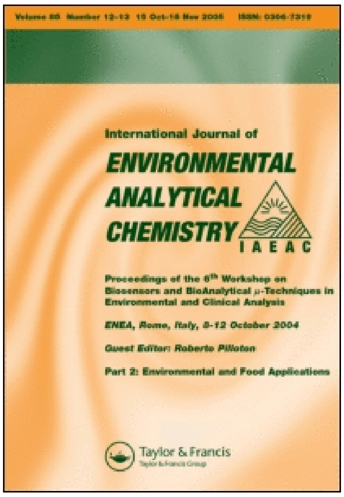

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Estimation of *N*-ethyl *O*-isopropyl Thionocarbamate (Dow: 2-200) in Mine Wastes by GLC

R. F. Addison[a]
[a] Fisheries Research Board of Canada, Marine Ecology Laboratory, Bedford Institute of Oceanography, Nova Scoria, Canada

To cite this Article Addison, R. F.(1974) 'Estimation of *N*-ethyl *O*-isopropyl Thionocarbamate (Dow: 2-200) in Mine Wastes by GLC', International Journal of Environmental Analytical Chemistry, 3: 4, 287 — 292
To link to this Article: DOI: 10.1080/03067317408071089
URL: http://dx.doi.org/10.1080/03067317408071089

Intern. J. Environ. Anal. Chem., 1974, Vol. 3, pp. 287–292

Printed in Great Britain

Estimation of *N*-ethyl *O*-isopropyl Thionocarbamate (Dow: Z-200) in Mine Wastes by GLC†

R. F. ADDISON

Fisheries Research Board of Canada, Marine Ecology Laboratory,
Bedford Institute of Oceanography, Dartmouth, Nova Scotia, Canada

(*Received November 27, 1973*)

KEY WORDS: Gas chromatography, Dow Z-200, mine wastes, ethyl isopropyl thionocarbamate

Dow Z-200 is a selective ore flotation agent, consisting mainly of *N*-ethyl, *O*-isopropyl thionocarbamate (IPETC). This paper describes a GLC method for the estimation of IPETC, and compares it with the conventional u.v. spectrophotometric procedure.

An aliquot of a cyclohexane extract of IPETC (prepared for spectrophotometric analysis) is chromatographed on a column of SE-30 or OV-17/QF-1 at 125°C and the IPETC peak is estimated in a ^{3}H electron capture detector (ECD). The ECD is superior in sensitivity and linearity of response to the flame photometric detector operated in the S-mode. The ECD-GLC procedure is comparable in sensitivity to the conventional u.v. absorbance method, and offers an independent and complementary procedure useful for confirmation of low levels of IPETC.

INTRODUCTION

N-ethyl *O*-isopropyl thionocarbamate (trivially isopropylethylthionocarbamate: IPETC) is the major component of Z-200 (Dow Chemical Co.), a flotation agent used in the mining industry. It is routinely estimated by u.v. absorbance after isolation by extraction into cyclohexane.[1] During a survey of process reagent levels in mine waste waters from Northeastern New Brunswick,[2] we consistently encountered apparent concentrations of

---

† Presented at the Symposium on Recent Advances in the Analytical Chemistry of Pollutants, Halifax, N.S., August 23–25, 1972.

IPETC in the low ppm range, which is close to background for the u.v. procedure. In order to confirm its presence at these levels, an independent analytical method seemed desirable. Its low b.p. (85°C/4 mm Hg)[1] suggested that it could readily be isolated by GLC, and its structure suggested that it should give responses on the electron capture detector (ECD) and the flame photometric detector (FPD) operated in the S-mode. This paper describes the development of a GLC method for the analysis of IPETC.

EXPERIMENTAL

IPETC was prepared by distillation of Z-200 (a gift of the Dow Chemical Co.) under reduced pressure. The main fraction came over at 110°C/8 mm Hg, and was colourless, in contrast to the pale yellow of the starting material. Its infrared spectrum (determined as a liquid film between NaCl plates on a Perkin–Elmer 700 instrument) showed strong bands at 1550 and 1240 cm^{-1} attributable to the —CS—NH—structure, and a band at 1140 cm^{-1} attributable to $=C=S$.[3] Its u.v. spectrum showed a peak at 247 nm (cyclohexane) with a molar absorptivity (assuming MW of 147) of 14,900 $\text{l mol.}^{-1}\ \text{cm}^{-1}$. Micro-analysis yielded the following elementary composition:

Calculated: C: 49.0%, H: 8.8%, N: 9.5%, O: 10.9%, S: 21.8%
Found: C: 48.5%, H: 8.9%, N: 10.2%, O: 11.3%, S: 21.2%

This preparation closely resembled that obtained by Jones and Woodcock,[1] and was used for all subsequent work.

GLC was carried out on two systems: (1) a Packard 7400 instrument fitted with a 6′ × 1/8″ (i.d.) (183 × 0.32 cm) glass column packed with 1.5% OV–17/2% QF-1 on 100–120 mesh Gas Chrom Q, operated at 125°C; carrier, He at 40 ml/min; injection port, 165°C; detector, ^{3}H–ECD at 210°C; (2) a laboratory-built instrument fitted with a 6′ × 1/8″ (i.d.) (183 × 0.32 cm) glass column packed with 3% SE–30 on 100–120 mesh Gas Chrom Q operated at 125°C; injection system, 170°C; detector, Melpar FPD with 394 nm filter, operated with gas flows according to the manufacturer's instructions. Peaks were recorded on Honeywell recorders and injections were made with Hamilton 701 N syringes. Calibration curves relating peak height response to load were constructed.

U.v. estimation of IPETC was carried out as described by Jones and Woodcock.[1] Solutions of standard IPETC, or extracts of field samples, were prepared in cyclohexane (Baker, Spectranalyzed) and read at 247 nm in a Unicam SP–500 instrument fitted with 1-cm quartz cells.

Ten-millilitre water samples (pH 7) taken from lakes in the Dartmouth area (used for recreational purposes only, and presumed to contain no

IPETC) were spiked with aqueous solutions of IPETC and extracted by shaking with equal amounts of cyclohexane. The extracts were subjected to u.v. and GLC analysis without further treatment. Mine waste samples (pH 5–7) were shipped to the laboratory in polyethylene bottles and allowed to settle; the supernatant (10 ml) was extracted with equal amounts of cyclohexane, generally within two days of sampling.

RESULTS AND DISCUSSION

Chromatography of cyclohexane solutions of standard IPETC under the conditions described above resulted in elution of a single peak attributable to IPETC within 2 min of injection. Slight tailing was evident on the OV–17/QF–1 column. A temperature-programmed run on this column (from 60° to 200°C at 10°C/min) did not reveal any other peaks.

The FPD response to IPETC was less efficient than that of the ECD. Minimum detectable amounts (for a peak twice as high as noise level) were approx. 40 ng and 1 ng, for the FPD and ECD, respectively. For a 5-mcl injection and 1:1 sample: extractant ratio, these correspond to minimum detectable sample concentrations of 8 and 0.2 ppm, respectively. Increasing the $O_2:H_2$ ratios in the FPD flame may improve the FPD response somewhat,[4] but seems unlikely to bring it close to that of the ECD. However, the relative specificity of the FPD towards S-containing compounds may be an advantage in some circumstances. As has been noted for other S-containing compounds,[4] the FPD response to IPETC increased with fairly high powers of load (3–4), whereas in load range 1–10 ng, the ECD response (peak height versus load) was approximately linear.

Extraction of IPETC from water samples into cyclohexane has been reported to be reasonably efficient, with over 90% being recovered in one manipulation using equal volumes of sample and extractant.[1] The results of a series of recovery experiments performed on lake water spiked with IPETC generally confirm this (Table I). Extracts of unspiked water showed no significant absorbance at 247 nm and GLC of these extracts showed no peaks interfering with that attributed to IPETC. (Cyclohexane itself gave rise to a small peak eluted about 0.5 min after the main solvent peak, but this did not interfere with IPETC estimation.) GLC of extracts of spiked lake water showed peaks corresponding in retention time to that of IPETC, and estimates of IPETC concentration derived from these peaks generally agreed closely with those made from u.v. absorbance measurements (Table I). Some fluctuation in recovery was observed, mostly at lower concentrations, using both u.v. and GLC methods; this was attributable to errors arising from measurement of low absorbances and small peaks.

TABLE I

Extraction by cyclohexane of lake water (pH 7.0) spiked with *N*-ethyl *O*-isopropylthionocarbamate

Conc. in water (ppm)	Conc. in cyclohexane extract (ppm)	
	u.v. method	GLC method
0	0	0
1.31	1.2 (92%)	1.5 (115%)
2.62	2.8 (107%)	2.4 (92%)
3.93	3.85 (98%)	3.7 (94%)
6.56	6.1 (93%)	6.2 (94%)
10.5	10.0 (95%)	10.7 (102%)
26.2	24.4 (93%)[a]	24.1 (92%)[a]
	1.2 (4.6%)[b]	1.0 (4%)[b]
Mean % recovery ± S.D.:	97.1 ± 5.4	98.8 ± 8.6

[a], [b] First and second extracts.

Cyclohexane extracts of samples of waste water from the copper, lead and zinc mining operations in Northeastern New Brunswick generally showed some u.v. absorbance at 247 nm, suggesting the presence of IPETC. Analysis of these samples for dithiocarbonates (xanthates), which also absorb in this region, showed that these compounds were virtually absent.[2] Chromatography of these samples showed a peak with retention time similar to that attributed to IPETC in standards (Figure 1). Estimates of IPETC concentration by both u.v. and GLC methods generally agreed to within about 20% (Table II).

As noted above, IPETC is not the only component of Z-200; *O*-isopropyl *S*-methyl dithiocarbonate (*O*-isopropyl methyl xanthate), *N*-ethyl dithiocarbamate, dimethyl trithiocarbonate, and *O*-isopropyl *S*-ethyl thionocarbamate may also be present.[5] Of these components, only dimethyl trithiocarbonate appears to have been subjected to GLC,[6] but the chromatographic conditions required, and the behaviour of this compound were not recorded. The extent to which these compounds may interfere with IPETC estimation is therefore unknown. However, GLC of the two samples of Z-200 available for this work contained no obvious peaks other than that of IPETC using either FPD or ECD, and since this compound is the main component of Z-200, the potential interference of other components in its estimation may not be a problem in practice.

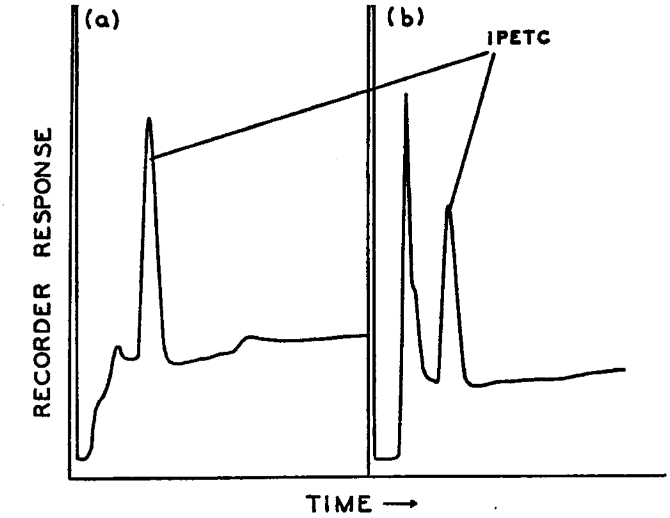

FIGURE 1 Chromatograms of (a) cyclohexane solution of IPETC and (b) a cyclohexane extract of mine waste water, on OV-17/QF-1. Conditions as described in text.

TABLE II

Comparison of u.v. and GLC determinations of IPETC in field samples.

	IPETC (ppm)	
Sample No.	u.v.	GLC
29	1.80	1.62
35	1.23	1.16
39	1.51	1.24
43	1.50	1.45

On the basis of the data presented here, it appears that ECD–GLC offers an alternative method to u.v. absorbance measurements for IPETC analysis. In practice, it is unlikely to be any more convenient than the u.v. method for routine analysis, but it offers an independent and complementary procedure which may be useful where confirmatory evidence is required.

References

1. M. H. Jones and J. T. Woodcock, *Proc. Aust. Inst. Min. Met.* **231,** 11 (1969).
2. R. F. Addison, L. D. Schnare, and D. C. Gordon, *Fish. Res. Bd. Can. Tech. Rep.* No. 293 (1972), 12 pp.
3. L. J. Bellamy, *The Infrared Spectra of Complex Molecules* (Methuen, London, 1958) 2nd ed., Chap. 22.
4. A. I. Mizany, *J. Chromatogr. Sci.* **8,** 151 (1970).
5. G. H. Harris and B. C. Fishback, U.S. Pat. 2691635 (1954); *Chem. Abst.* **49,** 1169e (1955).
6. J. M. Lalancette, Y. Beauregard, and M. Bhereur, *Can. J. Chem.* **48,** 1093 (1970).