1,1,2-Trichloro-1,2,2-Trifluoroethane for Oilseed Extractions

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ABSTRACT

1,1,2-Trichloro-1,2,2-trifluoroethane has been evaluated as a nonflammable, low toxicity extractant in oilseeds in comparison with petroleum ether, cyclopentane, and carbon tetrachloride. Full fat and defatted soybean flake were analyzed for oil content, free fatty acid, and total fat. 1,1,2-Trichloro-1,2,2-trifluoroethane appears to be generally acceptable for oilseed analyses. Small, but statistically significant differences were found between solvents which were not explainable on the basis of physical parameters.

INTRODUCTION

Petroleum ether (AOCS Specification H-241, boiling range 37.7-50.0 C), the usual solvent of choice in extractive analyses of oilseeds (1), and carbon tetrachloride, a substitute in some methods (2), suffer respectively from flammability (flash point -45.6 C) and toxicity (threshold limit value [TLV] = 10 ppm) (3-5). These deficiencies prompted an examination of 1,1,2-trichloro-1,2,2-trifluoroethane (nonflammable, TLV = 1,000 ppm) as an alternative solvent on safety considerations. Use of this solvent for oilseed extraction is not new. In 1955, Kaufman and vom Orde (6) compared this solvent with hexane for soybean oil extraction and reported similar results with the 2 solvents.

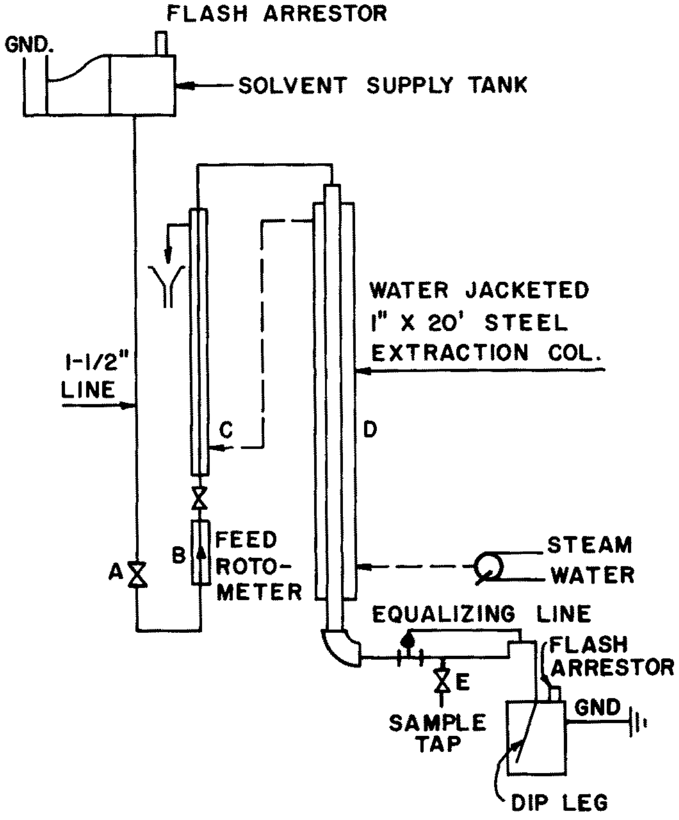

FIG. 1. A = Metering valve; C = preheater; E = sample tap; gnd = ground.

EXPERIMENTAL PROCEDURES

General

Full fat soybean flake was obtained from the A.E. Staley Co. (Decatur, IL). Defatted flake was prepared in the apparatus shown in Figure 1. Solvent was gravity fed through metering valve A, rotameter B, and then through preheater C before being fed through the extraction column D and sampled at tap E. It was noted during the course of our investigations in this apparatus that high fluorocarbon flow rates could be achieved without plugging or compacting the flake bed, and there was evidence of flake fluidization. High hexane flow rates always led to plugging or channeling in the flake bed. These results were a natural consequence of flake density being intermediate between the density of 1,2,2-trichloro-1,2,2-trifluoroethane and that of hexane.

The data on defatted flake given in this report are for extractions with hexane at 55 C and trichlorotrifluoroethane at 47 C (reflux) and identical volumetric solvent flow rates and volumes.

All oil and oil residue analyses were corrected for retained solvent, as measured by gas liquid chromatography (GLC). In almost all cases, the solvent remaining in oil samples evaporated to constant wt was low enough to be ignored and would not affect the gravimetric procedures.

GLC analyses were carried out on a Perkin Elmer 990 gas chromatograph using a 15 ft x 1/8 in. outside diameter stainless steel column packed with OV-101 polydimethylsiloxane, 10% by 25, on Chromosorb W-HP. This packing is commercially available from Chromatography Associates (Wilmington, DE). In practice, a 6 in. precolumn of the same material was used and daily changes of the injection port liner and septum were necessary to protect the main column from oil pyrolysis products.

Residual n-hexane in oil was determined by mixing 1.0±0.001 g of oil with 1.0 ml of an internal standard consisting of 0.2 mg/ml of 1,1,2-trichloro-1,2,2-trifluoroethane in 2,2,4-trimethylpentane (chromatoquality), and sampling 5 μl for GLC. Commercial hexane and petroleum ether could also be determined by this method by analyzing the composition of the solvent by GLC, calculating the relative areas of the component peaks, compared to n-hexane, and correcting for this in the final oil analysis.

Residual trichlorotrifluoroethane in oil was determined in similar fashion using an internal standard containing 0.02 mg/ml of n-hexane in 2,2,4-trimethylpentane. Analyses were run at a column temperature of 60 C using a flame ionization detector, a detector temperature of 150 C, an injection port temperature of 85 C, and a helium flow of 20 ml/min.

TABLE I

Oil, Full Fat Soybean Flake

Extractant	Number of replicates	Mean ± S.D.[a]	Sum of squares
Petroleum ether	4	18.40 ± 1.711	1362
$CFCl_2CF_2Cl$	4	18.37 ± 1.191	1354

[a] Variance between means, $S_b^2 = 0.0016$; variance within means, $S_w^2 = 2.17$; $F = S_b^2/S_w^2 = <1$.

TABLE II

Oil, Extracted Soybean Flake

Initial extractant	Analytical extractant	Number of replicates	Mean ± S.D. (%)	Sum of squares
Hexane	Petroleum ether	6	0.99 ± 0.253	6.18
Hexane	$CFCl_2CF_2Cl$	6	1.41 ± 0.113	11.94
$CFCl_2CF_2Cl$	Petroleum ether	12	1.94 ± 0.307	46.16
$CFCl_2CF_2Cl$	$CFCl_2CF_2Cl$	6	2.77 ± 0.267	46.50
$CFCl_2CF_2Cl$	Cyclopentane	8	2.41 ± 0.166	46.61

TABLE III

Analysis of Variance, Extracted Flake

Comparison	Variance between means	Degrees of freedom	Variance within means	Degrees of freedom	F	Critical F-value
Between initial solvents	20.2	1	0.07	33	289	1% 7.5 5% 4.2
Hexane extracted flake; petroleum ether $CFCl_2CF_2Cl$	1.20	1	0.039	10	30.8	1% 10.0 5% 4.96
$CFCl_2CF_2Cl$ extracted flake; petroleum ether $CFCl_2CF_2Cl$	2.78	1	0.087	16	32.0	1% 8.53 5% 4.49
$CFCl_2CF_2Cl$ extracted flake; $CFCl_2CF_2Cl$ cyclopentane	0.46	1	0.045	12	10.2	1% 9.33 5% 4.75
$CFCl_2CF_2Cl$ extracted flake; petroleum ether cyclopentane	1.06	1	0.068	18	15.6	1% 8.28 5% 4.49

TABLE IV

Free Fatty Acid (as Oleic Acid)

Extractant	Potentiometric method[a] Mean ± S.D.[b] (%)	AOCS method[c] Ca-5a-40 Mean ± S.D.[c] (%)
Petroleum ether	1.98 ± 0.05	2.28 ± 0.04
Trichlorotrifluoroethane	1.88 ± 0.05	2.28 ± 0.05

[a] Titration with tetrabutyl ammonium by hydroxide.

[b] Four replicate extractions, 10 g flake samples.

[c] Duplicate determinations.

Solvents

1,1,2-Trichloro-1,2,2-trifluoroethane was Freon® TF solvent (E.I. du Pont de Nemours and Company, Wilmington, DE) and was 99% pure by GLC. Petroleum ether (Fisher Scientific Co., King of Prussia, PA, stock no. E-139) met AOCS Specification H-241. Carbon tetrachloride (Fisher Scientific Co., King of Prussia, PA, certified grade, stock no. C-570) was 99 mole % pure. Cyclopentane, obtained from Phillips Petroleum Company (Bartlesville, OK), also was 99 mole % pure. Normal hexane (Ashland Chemical Co., Ashland, KY) contained 47-48% n-hexane and had a boiling range of 64-70 C.

Apparatus

Butt type extractors were obtained from Scientific Glass Apparatus Co. (Bloomfield, NJ). All weighings were made to within 1 mg of an Ainsworth 23NT balance.

Methods

Oil. Soy flake samples were ground with a porcelain mortar and pestle and sieved through US 20-35 mesh sieves. Sieved meal samples, 10.000±0.001 g, were placed in 30-cm Whatman No. 2 filter paper folded as described in AOCS Official Method Ba-3-38 (1). The sample envelope was enclosed in a second piece of Whatman No. 2 paper and placed in the tared Butt extractor and extracted with 50 ml of either petroleum ether, trichlorotrifluoroethane, or cyclopentane for 3 hr in a water bath. The water bath temperature was adjusted to give a reflux rate of ca. 150 drops/min. Reflux rate temperatures (uncorrected) were measured by inserting Adjustatherm® thermometers, 0-150 C range, 11½ in. long (Lab Glass, Inc., Vineland, NJ, catalog no. LG-105-11) through the top of the condensers. Refluxate temperatures averaged 38.8 C for petroleum ether, 47.0 C for trichlorotrifluoroethane and 47.5 C for cyclopentane. Solvent was evaporated from the extracts in a steam of dry nitrogen. Then, in a deviation from AOCS Method Ba-3-38 (1), the residual oil was transferred to tared aluminum weighing dishes (57 mm diameter x 10 mm ht) using the same solvents. The rinse solvents were then evaporated until no solvent odor remained, and finally evaporated to constant wt using a vacuum oven at 40 C and ca. 25 psig vacuum with a slight bleed of dry nitrogen. The residual oil from this determination was saved for determination of free fatty acid and for determination of residual solvent by GLC.

Free fatty acid. The oil samples from full fat flake were sampled for titration. Because of the small amount of

TABLE V

Iodine Number

Extractant	Mean ± S.D. (%)
Petroleum ether	126 ± 0
Trichlorotrifluoroethane	123 ± 1.41

TABLE VI

Total Fat Analysis of Full Fat Soybean Flake After Acid Digestion

Analytical extractant	Number of replicates	Mean ± S.D.	Sum of squares
Petroleum ether	6	17.02 ± 1.002	1744
$CFCl_2CF_2Cl$	6	14.87 ± 2.015	1347
CCl_4	4	17.67 ± 0.638	1250

sample available, the method chosen was one used routinely for microdeterminations of acid (7). Oil samples, 1.0000±0.5000 g, were dissolved in 50 ml of 90% aqueous acetone and titrated with 0.1054 N tetrabutyl ammonium hydroxide (in methanol) using a Metrohn® automatic titrator (Brinkman, Inc., Westbury, NY).

Ground full fat flake 20-35 mesh (70 g) were placed in Whatman extraction thimbles (43 x 123 mm) and extracted with petroleum ether or trichlorotrifluoroethane for 3 hr using Butt extractors as described above. The extracts were transferred to tared aluminum weighing dishes by using the same solvents and were evaporated to constant wt as before. The oil samples were analyzed for free fatty acid (as oleic) as described in AOCS Official Method Ca-5a-40 (8) and also for residual solvent by GLC.

Total fat. Standard Analytical Method B-20 of the Member Companies of Corn Refiners Association (2) for fat in cornstarch was adapted to soy flake. Full fat soy flake was ground with a mortar and pestle to 20-35 mesh sieve size. Samples (25±0.001 g) were suspended in 100 ml deionized water in 600-ml beakers, and 300 ml HCl aqueous (100 ml conc. HCl/200 ml deionized H_2O) was added with stirring. The suspension was heated to boiling with stirring and digested at the boil until a negative starch test was obtained with aqueous iodine solution. The beakers were then placed in an ice water slush and cooled to room temperature. The contents of the beakers were filtered through Whatman No. 1 paper and rinsed and washed with deionized water until ca. pH 5 was reached. After being dried overnight, the papers were placed in Whatman extraction thimbles (43 x 123 mm) which were placed in the Butt extractor and extracted with petroleum ether, CCl_4, or trichlorotrifluoroethane. A water bath was used for heating with petroleum ether and trichlorotrifluoroethane, but an oil bath was used with CCl_4. The refluxate temperatures were measured as described above, and no difference was seen for the petroleum ether or trichlorofluoroethane. The refluxate of CCl_4 had a temperature of 69 C.

RESULTS

Results are not corrected for percent moisture on flake. The results in Table I indicate that the precision of the analysis is not high enough to permit distinguishing between the 2 extractants. Tables II and III give results and variance analysis of residual oil in extracted flake, respectively. Table IV gives the result of free fatty acid (FFA) of oil extracted from full fat flake with trichlorotrifluoroethane and petroleum ether. The results of both methods (Table IV) differ by 0.1% or less between means, which is within the accepted precision of either method. Iodine number (Table V) was determined on oil from full fat flake by standard procedure (ICl in acetic acid) from duplicate extractions. The differences are statistically significant. The statistical significance no doubt arises from the exact replication obtained with the petroleum ether extraction. Tables VI and VII give results in "Total Fat" (by acid digestion) employing different extractants, those in present use and trichlorotrifluoroethane.

DISCUSSION

1,1,2-Trichloro-1,2,2-trifluoroethane is quite similar to hydrocarbon solvents in many of its physical properties and would be expected to behave similarly as an oil extractant.

TABLE VII

Analysis of Variance: Total Fat Analysis of Full Fat Soybean Flake After Acid Digestion

Comparison	Variance between means	Degrees of freedom	Variance within means	Degrees of freedom	F	Critical F-value
$CFCl_2CF_2Cl$; petroleum ether	14.0	1	2.55	10	5.49	1% 10.04 5% 4.96
$CFCl_2CF_2Cl$; CCl_4	19.0	1	2.69	8	7.06	1% 11.26 5% 5.32
Petroleum ether; CCl_4	2.0	1	0.81	10	2.46	1% 10.04 5% 4.96

TABLE VIII

Comparative Physical Properties of Extractants

	$CFCl_2CFCl_2$	Hydrocarbons	CCl_4
Solubility parameter[a]	7.3	7-8	8.6
Viscosity (centistokes, 25 C)[b]	0.65	~0.3	0.89
Density (g/ml, 25 C)[c]	1.56	0.63-0.66	1.59
Surface tension (dynes/cm, 25 C)[d]	17.1	17-18	26

[a] See Ref. 9.

[b] See Ref. 10.

[c] See Ref. 11.

[d] See Ref. 12.

Table VIII gives some comparative physical properties of common extractants and trichlorotrifluoroethane.

Kaufman and vom Orde found significant rate differences in the Soxhlet extraction of soybean chips with hexane and trichlorotrifluoroethane. A graphical reinterpretation of their work (Fig. 2) shows a strong temperature dependence on the results. This conlcusion is borne out by further work in our laboratory and is shown, in part, by the highly significant F-ratio between initial solvents (Table III). It was expected that trichlorotrifluoroethane (bp 47 C) would give about the same results, or possibly higher results than petroleum ether (boiling range 37.7-50.0 C). This would appear to be a logical explanation of the results in Tables II and III. As a check on this hypothesis, cyclopentane (bp 49 C) was also used as an extractant. The results obtained with cyclopentane are much closer to those obtained with trichlorotrifluoroethane than to those obtained with petroleum ether, but statistically different from either solvent. Other physical parameters undoubtedly play a role in the rate of extraction, particularly since the "oil" reported also contains nontriglyceride materials, including the phospholipid and other more tightly-bound fractions. Work in our laboratory using light scattering techniques has shown that soy lecithins obtained from various commercial sources behave differently in terms of diffusion, micelle size, and shape in hexane and trichlorotrifluoroethane solvent, particularly when the water content of the system is varied. In addition, residual oil from trichlorotrifluoromethane extracted flake usually gave a higher phosphorus analysis although, here again, hydration appeared to play a role. Not surprisingly, it was found that polar components, like lecithin, exist in solution as supermolecular aggregates whose behavior is not yet completely understood.

Free fatty acid analyses and iodine values on oil from full fat flake extracted with either petroleum ether or trichlorotrifluoroethane were very close, if not identical.

The results obtained upon extraction of the residues of acid hydrolyzed material are not explainable at this time, particularly in light of the previous results. There is some indication of a statistically significant different between trichlorotrifluoroethane and both petroleum ether and CCl_4. Infrared analyses of the extracted oil failed to show any major difference, and GLC analysis for residual solvent showed levels too low to affect the gravimetric results. This discrepancy is worth further investigation.

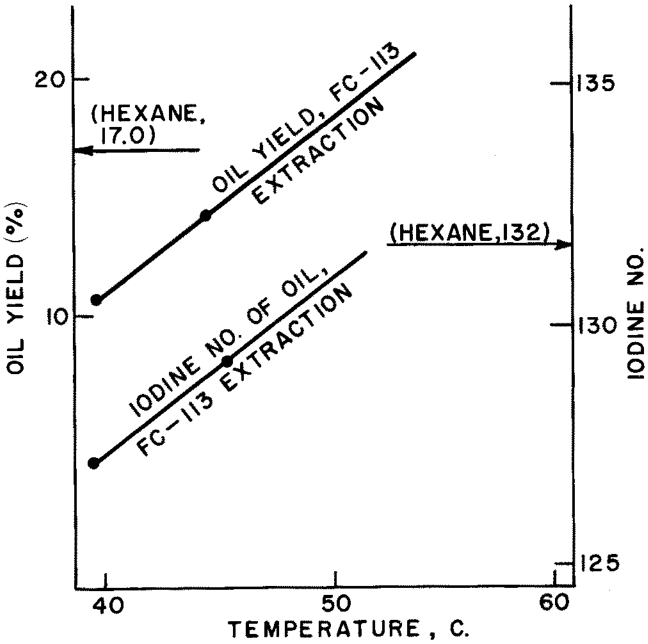

FIG. 2. Graphical interpretation of data of Kaufman and vom Orde on 5-hr extraction.

ACKNOWLEDGMENTS

R.J. Troy and R. DeGeiso developed the GLC techniques for solvent residues.

REFERENCES

1. "Official and Tentative Methods of the American Oil Chemists' Society," Vol. I and II, Third Edition, AOCS, Champaign, IL, 1964 (revised to 1972), Method Ba-3-38.
2. "Standard Analytical Methods of the Member Companies of the Member Companies of the Corn Refiners Association, Inc.," Vol. I, Corn Refiners Association, Washington, DC, Nov. 14, 1955, Method B-20.
3. American Conference of Government Industrial Hygienists, "Threshold Limit Values for Chemical Substances and Physical Aspects in the Workroom Environment, with Intended Changes for 1973," Cincinnati, OH, p. 13.
4. Ibid., p. 31.
5. Ibid., p. 38.
6. Kaufman, H.P., and H.O. vom Orde, Fette Seifen Anstrichm. 57:399 (1955).
7. Peers, K.H., Chemistry and Industry 11:455 (1974).
8. "Official and Tentative Methods of the American Oil Chemists' Society," Vol. I and II, Third Edition, AOCS, Champaign, IL, 1964 (revised to 1972), Method Ca-5a-40.
9. Burrel, H., and B. Immergut, in "Polymer Handbook," Edited by J. Brandrup and W.H. Immergut, Interscience, New York, NY, 1967, p. 341.
10. Elias, H.G., and F.W. Ibrahim, Ibid., p. 29.
11. Timmermans, J., "Physico-chemical Constants of Pure Organic Compounds," Vol. 1, Elsevier, NY, 1950, p. 224.
12. "Physical Properties of Chemical Compounds – II," Edited by R.R. Dreisbach, Chemical Society Advances in Chemistry Series, No. 22, Washington, DC, 1959.

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