

[Regular Paper]

A Comparison between Extractant Solvents in the Quantitative Analysis of Total Petroleum Hydrocarbons in Soil Samples

Saman C. BUDDHADASA^{†1)}, Sebastian BARONE^{†1)}, Stephen W. BIGGER^{†2)}, and John D. ORBELL^{†2)*}

^{†1)} Australian Government Analytical Laboratories (AGAL), 51-65 Clarke St., South Melbourne, Victoria 3205, AUSTRALIA

^{†2)} School of Molecular Sciences, Victoria University, P. O. Box 14428, Melbourne City MC, Victoria 8001, AUSTRALIA

(Received March 28, 2002)

Any given method for the analysis of semi-volatile total petroleum hydrocarbons (TPH, C₁₀-C₃₆) in contaminated soil is made up of a number of procedures, each of which may be subject to improvement or optimization. One such procedure involves the extraction of TPH from soil samples using an appropriate solvent. A solvent that is widely used is dichloromethane (DCM). Ideally, the chosen solvent should represent the best compromise between factors such as cost, extraction efficiency and occupational health and safety concerns. We have initiated a search for alternatives to neat DCM which are equally efficient at solubilising TPH over a range of soil types, but which are less expensive to purchase and dispose of, and which are less toxic. Two studies were carried out involving the analysis of TPH levels in a total of 78 field samples, from a number of contaminated sites. For **Study 1**, TPH levels were determined for 36 samples (from five different sites), comparing the use of neat DCM *versus* 50%v/v DCM/acetone as extractant solvents. For **Study 2**, TPH levels were determined for 42 samples (from one site), comparing the use of 50%v/v DCM/acetone *versus* neat 2-propanol as extractant solvents. Apart from varying the extractant solvent, all other aspects of the method were kept constant. The soils were characterized for all samples, and the six sites were found to have similar moisture content and soil type distributions. Levels of TPH in the extracts were determined by gas chromatography with flame ionization detection (GC/FID) and, using the paired t-test, were statistically compared between each of the two pairs of extractant solvents used. These investigations suggest that for routine field samples, and for sites of the type represented here, 50%v/v DCM/acetone may be confidently substituted for neat DCM as an extractant solvent. However, 2-propanol is not recommended as a substitute for either 50% DCM/acetone or DCM.

Keywords

Total petroleum hydrocarbon, Contaminated soil, Extractant solvent, Dichloromethane, Acetone, 2-Propanol

1. Introduction

Crude petroleum is essentially a mixture of paraffinic, naphthenic and aromatic hydrocarbons with small amounts of sulfur, nitrogen and oxygen containing compounds¹⁾. Primary separation into various fractions, defined by their boiling point ranges, is carried out by distillation at numerous refineries around the world. These products are then stored, and distributed for further storage, at a variety of facilities including depots, terminals, automobile service stations and general industrial sites. Release of these products into the environment is common and soil contamination, in particular, occurs through surface spills (*e.g.* during product transfer) and/or by leaks from damaged or corroded underground service lines and storage tanks²⁾. The assessment of sites thus contaminated requires the reli-

able quantification of residual hydrocarbons in the soil³⁾. Within a given regulatory framework⁴⁾, such data may be used to make recommendations and decisions regarding site rehabilitation and development⁵⁾.

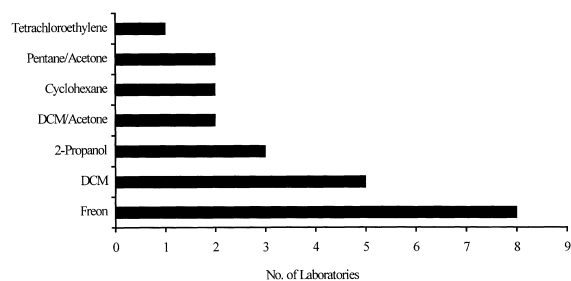
A widely used, albeit loosely defined⁶⁾, parameter for expressing the aggregate amount (mg kg⁻¹) of petroleum hydrocarbon compounds in a sample is the so-called TPH (total petroleum hydrocarbons)⁷⁾. The semi-volatile TPH parameter is considered to include hydrocarbons of chain length C₁₀-C₃₆⁸⁾. In Australia, at the national level, there are currently no guidelines or prescribed standard method for the determination of TPH levels in contaminated soils⁹⁾. A consequence of this is that different laboratories, although employing similar methods, might be varying the details of one or more of the composite procedures. For example, the choice of solvent used for the extraction of TPH from soil samples might be dictated by the need to cut costs or to reduce toxicity. A tabulation of relevant information relating to such matters as cost, properties,

* To whom correspondence should be addressed.

* E-mail: John.Orbell@vu.edu.au

Table 1 Comparative Properties for DCM, Propanone and 2-Propanol

Property	DCM Dichloromethane	Acetone Propanone	2-Propanol Popane-2-ol
Product name			
CAS number	75-09-2	67-64-1	67-63-0
Hazards identification	Possible risk of irreversible effects	Highly flammable, vapour/air mixture explosive Precaution against static discharge	Highly flammable, vapour/air mixture explosive Precaution against static discharge
Handling	Under no circumstances eat, drink or smoke while handling this material		
Form	Liquid	Liquid	Liquid
Colour	Colourless	Colourless	Colourless
Solubility in water	Slightly soluble	Miscible in all proportions	Miscible in all proportions
Flash point	Non flammable	-20°C	12°C
Stability	Stable	Stable	Stable
Toxicity	Carcinogen, category 3	No evidence of mutagenic or teratogenic effects.	No evidence of reproductive effects.
Ecological information	Has been found to cause cancer in laboratory animals. May cause mutagenic activity or teratogenic effects. Low bioaccumulation potential and aquatic toxicity.	No environmental hazard is anticipated if the material is handled and disposed of with due care. Residues are classified as special waste.	No environmental hazard is anticipated if the material is handled and disposed of with due care. Residues are classified as special waste.
Disposal consideration	Residues are classified as special waste requiring special disposal requirements.		
Price per 4 l (approximate)	\$A 40	\$A 35	\$A 50



Freon has recently been withdrawn from use.

Fig. 1 Results of a Survey of Extractant Solvent Use in Australian Analytical Laboratories

occupational health and safety concerns etc. for the three solvents used in this study is given in **Table 1**.

According to a recent survey carried out by the Victorian Environmental Protection Authority (VicEPA)⁹, most laboratories use DCM/acetone (50%v/v), 2-propanol or DCM, **Fig. 1**.

Thus 50%v/v DCM/acetone or neat 2-propanol are sometimes substituted for neat DCM. To our knowledge, the difference in the extraction efficiencies between these three solvent systems, in particular, has never been investigated. This study investigates the effect on TPH values of using 50%v/v DCM/acetone *versus* neat DCM and 50%v/v DCM/acetone *versus* neat 2-propanol for the analysis of TPH levels in samples from real contaminated sites. Such investigations will help in the development of a national standard test so that all laboratories can use the same, or equivalent, test methods. This will allow site assessors to have more confidence in analytical results obtained from different laboratories.

2. Experimental

2.1. Chemicals and Equipment

All chemicals (Crown Scientific, Melbourne, Australia) were of the highest grade. Ultrapure water was used throughout. All glassware was cleaned before use by soaking in a 2%v/v Pyroneg[®] (Diversey Levy, Australia) solution for approximately 8 h and in a 2%w/v chromic acid solution for a further 2 h. The glassware was then rinsed with water and acetone, and then air-dried. All pipettes and volumetric flasks were calibrated before use. Contaminated soils were stored at 4°C in 1 l screw-cap glass jars until the sub-sampling stage of analysis. Sub-samples were solvent extracted in 125 ml screw-cap glass jars with Teflon (PTFE) liners. Samples for gas chromatographic analysis were contained in 2 ml PTFE rubber-lined gas chromatographic (GC) glass vials (Proscience, Melbourne, Australia) with crimpable caps. The crimper (SGE Scientific, Australia) was designed specifically for

GC/FID work. A Branson 8210 ultrasonic bath (950 watt, 47 kHz), with a capacity to hold twenty extraction jars, was employed. Samples containing fine particles were centrifuged using a MSE Microcentaur.

2.2. Preparation of Standards

For calibrations, certified grade alkane standards, with purities >99% (Sigma-Supelco; Ultrascientific, Australia) were used. A stock solution of 10^4 ng μl^{-1} was prepared by weighing known quantities of *n*-C₉H₂₀, *n*-C₁₀H₂₂, *n*-C₁₂H₂₆, *n*-C₁₄H₃₀, *n*-C₁₆H₃₄, *n*-C₁₈H₃₈, *n*-C₂₄H₅₀, *n*-C₂₈H₅₈, *n*-C₃₀H₆₂, *n*-C₃₂H₆₈ and *n*-C₃₆H₇₄ into a 100 ml volumetric flask and making up to the mark with DCM. Calibration standards of 2 and 10 ng μl^{-1} and spiking standards of 25 and 1000 ng μl^{-1} (to conduct recovery studies for quality assurance) were prepared by appropriate dilution of the DCM stock¹⁰.

2.3. Sampling

Bulk samples were taken from a number of sites, known to be contaminated with TPH. For the analyses where DCM and DCM/acetone were used as extractant solvents (**Study 1**), 36 bulk samples of ca. 1 kg each were received from five former petrol station sites across Australia. For the analyses where DCM/acetone and 2-propanol were used as extractant solvents (**Study 2**), 42 bulk samples of ca. 0.25 to 0.50 kg each were received from the site of a former oil refinery. Prior to further characterization, all bulk samples were homogenized using a standard mortar and pestle technique¹⁰. For both **Studies 1** and **2**, seven 10 g sub-samples were taken from each of the homogenized bulk samples. Standard sub-sampling techniques were employed¹⁰⁻¹². Each set of seven sub-samples was processed as follows: **Study 1** (total of 36 sets, $7 \times 36 = 252$ sub-samples): *Sub-sample 1* – tested for soil type; *Sub-samples 2 & 3* – duplicate analysis for moisture content; *Sub-samples 4 & 5* – duplicate extraction in neat DCM; *Sub-samples 6 & 7* – duplicate extraction in 50%v/v DCM/acetone. **Study 2** (total of 42 sets, $7 \times 42 = 294$ sub-samples): *Sub-sample 1* – tested for soil type; *Sub-samples 2 & 3* – duplicate analysis for moisture content; *Sub-samples 4 & 5* – duplicate extraction in 50%v/v DCM/acetone; *Sub-samples 6 & 7* – duplicate extraction in neat 2-propanol.

2.4. Soil Types and Moisture Content

Sub-sample 1 for each of the 78 sets of samples in **Studies 1** and **2**, was characterized using the Northcote Bolus Manipulation Method¹³. *Sub-samples 2 & 3* (duplicates) for each of the 78 sets were analyzed for moisture content according to a standard procedure¹⁴. The distribution of different soil types over the 78 sub-samples, and moisture content data, are given in **Table 2**.

2.5. Solvent Extraction of Soil Samples

The following procedure was carried out for *Sub-*

Table 2 Soil Type Classification, Distribution and Moisture Content for the Selected Sub-samples

Soil type	Sub-sample classification		Moisture content	
	Study 1 ^{a)}	Study 2 ^{a)}	Study 1 ^{b)}	Study 2 ^{b)}
Sand	13	12	12.4	11.3
Clay	39	55	16.9	13.9
Sandy loam	48	33	13.1	9.9

a) % of total number of sub-samples. b) average % by weight.

samples 4 & 5 (respective duplicates) and *6 & 7* (respective duplicates) in both studies. To each of the soil sub-samples (10 g), contained in a 125 ml glass jar, was added 20 ml of the appropriate solvent; with rapid mixing to eliminate clumping. The jar was then placed in an ultrasonic bath, cooled with ice packs to a minimum of 10°C, and sonicated for 10 min. The extracts were dried over anhydrous sodium sulfate (ca. 5-10 g) while mixing well with a glass rod, and the samples were sonicated for a further 10 min. The soil was then allowed to settle from the solvent fraction. A portion of the supernatant was centrifuged at 13,000 rpm for 5 min or until the supernatant was clear. A sample of between 1-2 ml was transferred to a 2 ml glass crimp-top GC vial and crimped immediately to avoid evaporation. Each vial was set aside for subsequent GC/FID analysis. Samples were processed in batches of ten vials (five duplicates). For each batch one reagent blank and one soil blank analysis was carried out, and one recovery sample was analyzed. The soil blank was carried out using a “hydrocarbon free soil matrix” and the recovery sample was prepared by carefully spiking a soil blank with a known quantity of TPH. A recovery of between 80-100% was achieved, which is considered to be acceptable for such methods^{11,15}.

2.6. Semi-volatile TPH Analysis

All extracts were analyzed by a gas chromatography flame ionization detector method (GC/FID)^{9,10,15-17}. The instrument used was a Hewlett-Packard 5890 Series II fitted with a SGE BPX5 (25 m \times 0.22 mm I.D. \times 0.25 μm film thickness) column, a Hewlett-Packard 7673A auto sampler and HP Chemstation software. The parameters chosen were as follows: 325°C injector temperature, 350°C detector temperature, 175 kPa column head pressure, 40°C initial value for the oven temperature program, initial hold time of 0.8 min, temperature rate of 27°C min^{-1} up to 100°C and 35°C min^{-1} up to 350°C, final hold time of 5 min. The instrument was calibrated using the 2 ng μl^{-1} working standard, described previously. **Figure 2** shows the chromatogram obtained for the standards mixture.

The TPH (C₁₀-C₃₆) values were calculated on a moisture-free basis (mg kg^{-1}) using the integration events timetable facility of the HP Chemstation software.

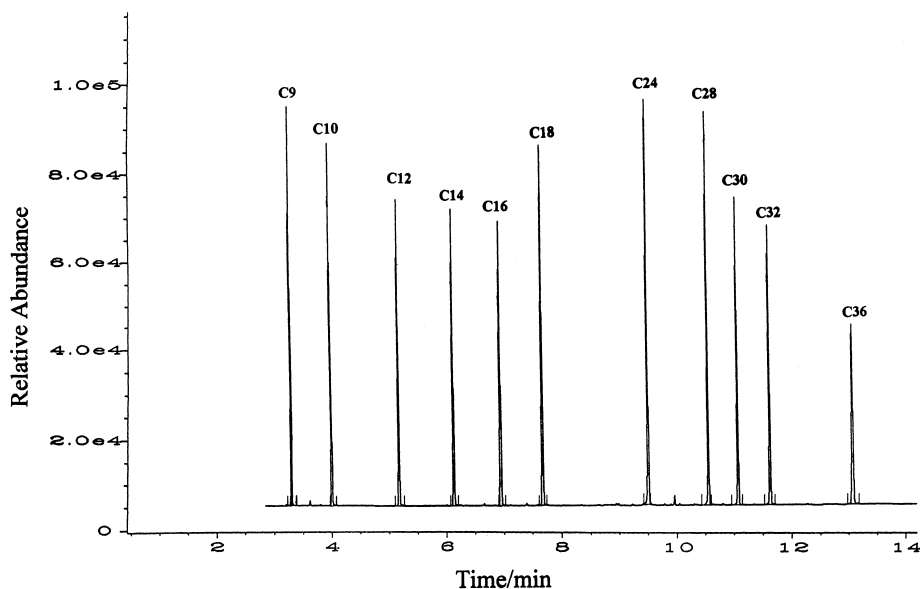


Fig. 2 Chromatogram for the TPH Standards

The data were recorded as duplicate averages. Concentrations at and above 75 mg kg^{-1} were used in the statistical analysis¹⁰.

3. Results

Figures 3(a) and 3(b) show chromatograms which are representative of the 72 (duplicate) procedures where extraction was carried out with DCM/acetone and DCM, respectively (Study 1).

Figures 4(a) and 4(b) show chromatograms which are representative of the 84 (duplicate) procedures where extraction was carried out with DCM/acetone and 2-propanol, respectively (Study 2).

Each TPH datum represents one such integrated profile over the C₁₀-C₃₆ range. Although such a datum is commonly referred to as the total petroleum hydrocarbon (TPH) content, and forms the basis for routine TPH analysis, it is actually a measure of the total extractable organic content of the sample under a given set of conditions¹⁸. Thus it can be seen from Figs. 3 and 4 that literally hundreds of unidentified components may be present. The comparative data for the 36 samples of Study 1 and the 42 samples of Study 2 are represented in Figs. 5 and 6, respectively.

The two sets of data were statistically analyzed using a paired *t*-test¹⁹ at the 0.05 probability level. The null hypothesis, that different extractant solvents do not lead to significantly different readings of THP values, is accepted for Study 1 [$t(\text{calc}) = 0.95 < t(\text{critical}) = 2.04$, $P = 0.05$, $n = 36$] and rejected for Study 2 [$t(\text{calc}) = 4.58 > t(\text{critical}) = 2.04$, $P = 0.05$, $n = 42$]. An F-test ($P = 0.05$) for the former study revealed no significant difference in precision between the two methods.

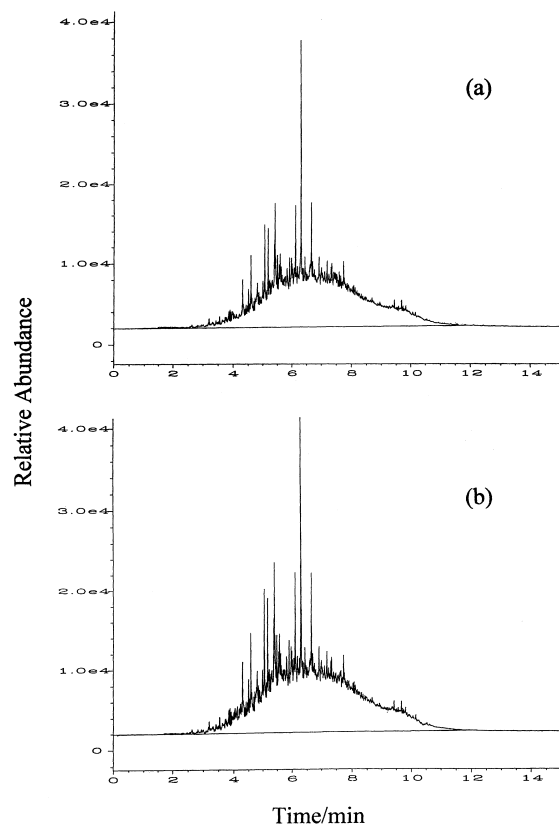
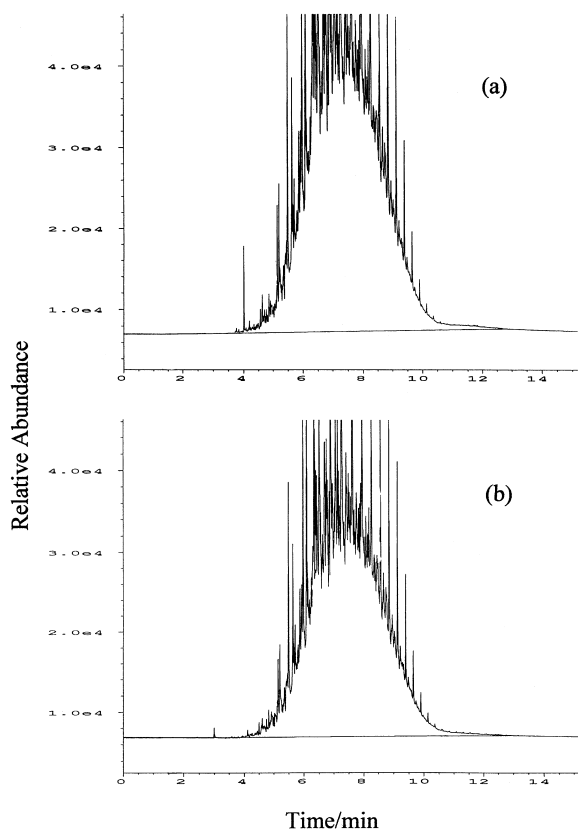


Fig. 3 Representative Chromatograms for TPH Extracted with (a) 50%v/v DCM/Acetone and (b) Neat DCM, Respectively

Raw data are available upon request.

Although soxhlet extraction has been demonstrated to be more effective in removing TPH from clay soil



The chromatograms are truncated at the top in order to save space.

Fig. 4 Representative Chromatograms for TPH Extracted with (a) 50%v/v DCM/Acetone and (b) Neat 2-Propanol, Respectively

compared to sonication extraction²⁰), this study applied sonication throughout, since the aim was to only to compare the effect of solvent on relative TPH extractability. It is anticipated that similar relative results would be attained by soxhlet, although this would have to be confirmed. For such large numbers of analyses, sonication is preferred for experiments of this kind. An additional consideration in this work is that this study and the study referred to²⁰), were carried out at approximately the same time and the opportunity did not exist to relate the outcomes of one to the other. In this investigation, soil type and moisture content have been carefully monitored to ensure that these variables are as well characterized as possible, **Table 2**. Our data suggests that for sand, clay and sandy loam, there is no significant influence for moisture contents up to 17% (by weight). Research is presently being carried out to further investigate the specific influence on TPH levels of soil type and moisture content, as well as the volume ratios of acetone and DCM used in TPH extraction.

4. Conclusion

The use of DCM *versus* 1 : 1 DCM/acetone is found to produce no significant difference in the extractable concentration of TPH. On the other hand, at the same level of confidence (95%), the use of 1 : 1 DCM/acetone *versus* 2-propanol results in significantly different extractable concentrations of TPH. These investigations suggest that for routine field samples, and for sites of the type represented here, 50%v/v DCM/acetone

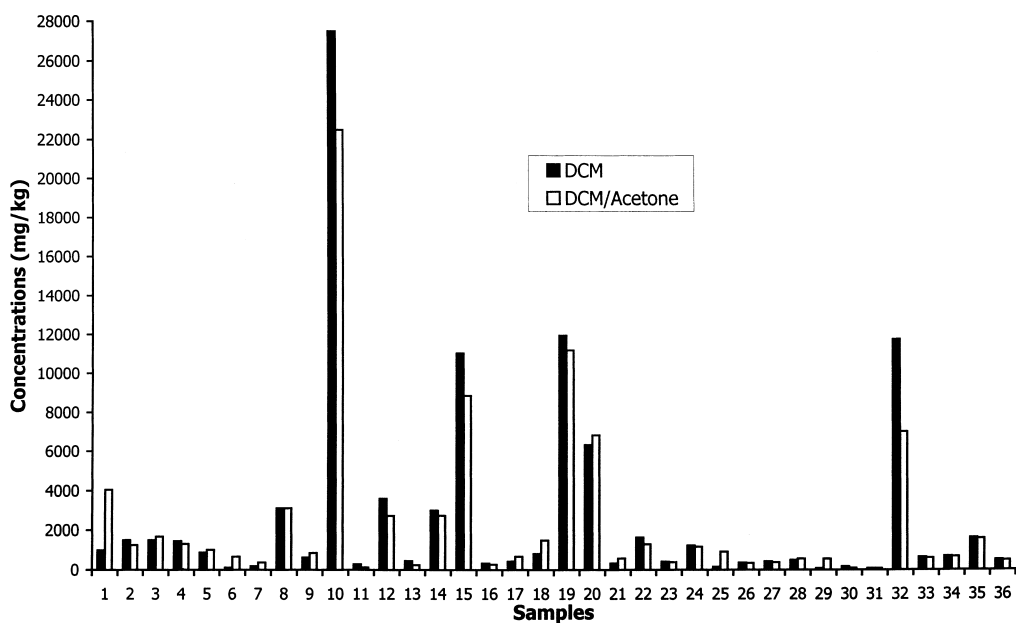


Fig. 5 Comparison of TPH (C₁₀-C₃₆) Concentrations Obtained with DCM and 50%v/v DCM/Acetone as Extractant Solvents

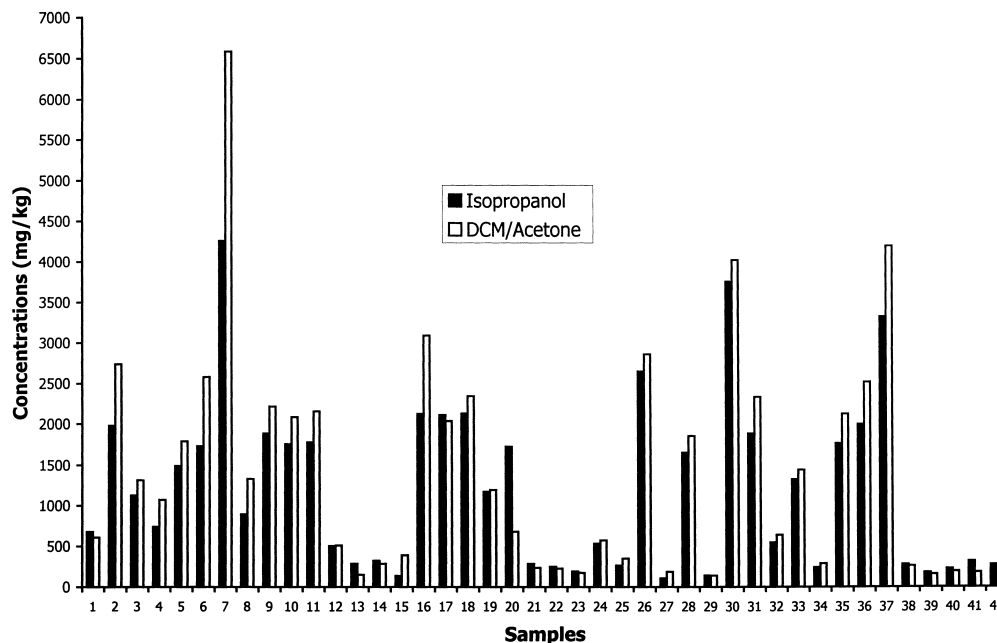


Fig. 6 Comparison of TPH (C_{10} - C_{36}) Concentrations Obtained with 2-Propanol and 50%v/v DCM/Acetone as Extractant Solvents

may be confidently substituted for neat DCM as an extractant solvent. However, 2-propanol is not recommended as a substitute for either 50%v/v DCM/acetone or DCM.

Acknowledgments

This work is part of the Australian Government Analytical Laboratories' (AGAL) Public Interest Program. The authors are grateful for AGAL's financial and technical support. Thanks are due to the following AGAL staff: Dr. Sandra Hart (Australian Government Analyst) and Dr. Brett Yeomans for their support and advice. We would also like to thank Dr. Rod Miller of the National Analytical Reference Laboratory (NARL) for his advice on statistical analysis.

References

- 1) "Handbook of Chromatography: Hydrocarbons," eds. by Gunter, Z., Sherma, J., CRC Press, Boca Raton, Florida, USA (1987), ch. 1.
- 2) "Analysis of Petroleum Hydrocarbons in Environmental Media," Vol. 1, ed. by Weisman, W., Amherst Scientific Publishers, Amherst, Massachusetts, USA (1998), p. 1-20.
- 3) "Guidelines for the Laboratory Analysis of Contaminated Soils," Australian and New Zealand Environment and Conservation Council, Canberra, ACT, Australia, August (1996), ch. 4.
- 4) National Environment Protection Measures (Assessment of Site Contamination), National Environment Protection Council Service Corporation, Adelaide, Australia, March (1999), Schedules B(1)-B(3).
- 5) Cole, G. M., "Assessment and Remediation of Petroleum-Contaminated Sites," CRC Press, Boca Raton, Florida, USA (1994).
- 6) Hutcheson, M. S., Pedersen, D., Anastas, N. D., Fitzgerald, J., Silverman, D., *Regul. Toxicol. Pharmacol.*, **24**, 85 (1996).
- 7) Guibo, G., Barcelona, M. J., Fang, J., *Anal. Chem.*, **71**, (9), 1899 (1999).
- 8) Carrell, B., "Semi-Volatile Petroleum Products Method for Soil and Water," Manchester Environmental Laboratory, Dept. of Ecology, Washington State University, USA (1997).
- 9) Good, J., Magor, J., Seignior, M., "A Review of Procedures Used to Measure Total Petroleum Hydrocarbons for Contaminated Site Assessments," Proceedings of the Combined 13th Australian Symposium on Analytical Chemistry, Royal Australian Chemical Institute, Darwin, Australia, July (1995).
- 10) Method VL228, "Determination of Total Petroleum Hydrocarbons and BTEX in Soil and Sediment by GC/FID," Australian Government Analytical Laboratories, Melbourne, Australia (1998), Issue 3.
- 11) "USEPA Publication SW846, Test Methods for Evaluating Solid Waste," 3rd. ed., Washington, DC (1999), ch. 4.
- 12) Coleman, W. E., *Arch. Environ. Contam. Toxicol.*, **13**, 171 (1984).
- 13) Northcote, K. N., "Australia. A Geography. Vol. 1, The Natural Environment," ed. by Jeans, D. N., (1986), p. 223-259.
- 14) Method VL237, "Preparation and Determination of Moisture Content in Soils," Australian Government Analytical Laboratories, Melbourne, Australia (1998), Issue 2.
- 15) Fan, C. Y., Krishnamarthy, S., Chien, T., "A Critical Review of Analytical Approaches for Petroleum Contaminated Soil," Lewis Publishers, Chelsea, Michigan, USA (1995).
- 16) Worrall, R., "Factors Affecting the Quantitation of Petroleum Hydrocarbons Using GC/FID," AGAL Public Interest Project 479, (1996).
- 17) Ilias, A., "Fuel Isolation, Identification and Quantitation from Soil," Proceedings of the West Coast Soils and Ground Waters Conference, Seattle, July 14-16, USA (1992).
- 18) Mills, M. A., McDonald, T. J., Bonner, J. S., Simon, M. A.,

- Autenrieth, R. L., *Chemosphere*, **39**, (14), 2563 (1999).
 19) "Statistics for Analytical Chemistry," eds. by Miller, J. C., Miller, J. N., 3rd ed., Ellis Horwood Ltd., Great Britain (1993), ch. 1-5.
 20) Buddhadasa, S. C., Barone, S., Bigger, S. W., Orbell, J. D., *J. Jpn. Petrol. Inst. (Sekiyu Gakkaiishi)*, **44**, (6), 378 (2001).

要 旨

土壌試料中の石油系炭化水素総量の定量分析における抽出用溶剤の比較

Saman C. BUDDHADASA^{†1)}, Sebastian BARONE^{†1)}, Stephen W. BIGGER^{‡2)}, John D. ORBELL^{‡2)}

^{†1)} Australian Government Analytical Laboratories (AGAL), 51-65 Clarke St., South Melbourne, Victoria 3205, AUSTRALIA

^{‡2)} School of Molecular Sciences, Victoria University, P. O. Box 14428, Melbourne City MC, Victoria 8001, AUSTRALIA

汚染土壌中の半揮発性石油系炭化水素総量 (Total Petroleum Hydrocarbon, TPH, C₁₀~C₃₆) の分析法は、改良または最適化を要する多くの手順から構成されている。その手順の一つが、適切な溶剤を使用して土壌試料から TPH を抽出することである。溶剤としてジクロロメタン (DCM) が広く用いられているが、理想的にはコスト、抽出効率、作業上の安全衛生を考慮して、最適な溶剤が選択されるべきである。本研究では、DCM と同等の抽出効率を有し、購入および廃棄コストが廉価で毒性の少ない代替溶剤について検討した。汚染場所から採取

した土壌 78 試料を用いて、2 種類の検討を行った。一つ目は抽出用溶剤として DCM と 50% v/v DCM/アセトン を土壌 36 試料で比較し、二つ目は 50% v/v DCM/アセトン と 2-プロパノールを土壌 42 試料で比較した。抽出物中の TPH は、FID 検出器付きガスクロマトグラフにより求めた。統計上の検定解析を行った結果、抽出用溶剤として DCM の代わりに 50% v/v DCM/アセトンを使用できることが示唆された。一方、2-プロパノールは、50% v/v DCM/アセトンや DCM の代用として推奨されない。