

# Isolation and Identity Verification of Polyalkylene Glycols in Fire Resistant Hydraulic Fluids Type C and D U

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## SYNOPSIS

A procedure to verify the identity of hydraulic fluids (HF) type C and D U is described. Different gel filtration systems were tested to separate the constitutive components. After fractionation of the mixture, IR and NMR spectroscopy were tried for their suitability in verifying the identity of the different constituents. The combination of aqueous gel filtration chromatography and IR spectroscopy was found suitable to separate and identify the different components of HFC fluids. For HFD U fluids, a modified gel filtration system was used and NMR spectroscopy was necessary to give a decisive answer about their identity.

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## INTRODUCTION

Following the prescriptions of the European Community,<sup>1</sup> a verification of identity is necessary on fire resistant hydraulic fluids (HF) to permit an assessment of the possible toxicity of these fluids and their pyrolysis products. For hydraulic fluids, type C (HFC) consisting of a mixture of polyalkylene glycols, lower glycols, and water, no proper verification procedure has been described so far. A method was studied to separate glycols by aqueous gel filtration chromatography. More recently, some new fluids were introduced and classified as hydraulic fluids type D U (HFD U). These nonaqueous fluids contain related polyalkylene glycols but are almost insoluble in water. An alternative gel filtration procedure was developed to include these liquids in the verification procedure.

The first literature of aqueous gel filtration chromatography appeared in the late seventies. A review was published by Cooper and Van Derveer<sup>2</sup> in 1978. Since the development of hydrophilic compounds chemically bonded with glass beads, high speed gel filtration became possible. Kato et al.<sup>3,4</sup> were some

of the first authors to report separation results in high-speed gel filtration. Callec et al.<sup>5</sup> described the use of Fractogel TSK gels in strong alkaline medium for the molecular weight identification of different polymers, including dextrans, polyethylene glycols, and sodium polystyrene sulfonates. Although these authors found the column efficiency satisfactory ( $N = 2500\text{--}8750$  theoretical plates/meter, calculated on the elution pattern of glucose), no results of resolution calculations were given, which makes it impossible to evaluate the separation adequacy. Furthermore, only a small range of polyethylene glycols was covered. This article examines in detail the suitability of three Fractogel TSK gels for the molecular weight identification over a wide range and separation of polyalkylene glycols present in HFC and HFD U. Some recently introduced gel filtration media, Superdex 75 prep grade and Superdex 200 prep grade, were also tested because Kagedal et al.<sup>6</sup> have demonstrated superior efficiencies of the latter for globular proteins and dextrans.

## EXPERIMENTAL

### Chemicals

Superdex 75 prep grade and Superdex 200 prep grade were supplied by Pharmacia LKB Biotechnology

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(Uppsala, Sweden). These gels were delivered prepacked in XK 16/60 columns. Fractogel TSK HW40(S) and Fractogel TSK HW65(F) were supplied by Merck (Darmstadt, Germany) and packed in the laboratory in XK 16/60 columns using the constant-flow packing technique. Fractogel TSK HW55(F) was supplied by Merck and packed in an XK 26/60 column.

Ethylene glycol ( $M_w$  62); polyethylene glycol standards of  $M_w$  106, 194, 440, 960, 1470, 4250, 7100, 12600, and 23000; and polyethylene oxide standards of  $M_w$  10300, 23500, 32500, 64700, 86500, 150000, 250000, 450000, 730000, and 1390000 were supplied by Polymer Laboratories (Essex, UK). Glissosafe® 610, Glissosafe® 602, Glissosafe® V102, and Pluracol V10 were supplied by BASF. Samples of Glykol I and Glykol II (experimental fluids), Hydraulic TR46® (Brenntag, Mineral Oel GmbH, Mülheim a.d. Ruhr), Isocor E46® (Theunissen GmbH, Wuppertal, Germany) were gifts from different sources.

### Gel Filtration

Gel filtration was carried out at 23°C. Bidistilled water was used as eluents for the analysis of HFC fluids and a mixture of water/acetonitrile (80/20) for HFD U fluids. The eluents were supplied at a flow rate of 40 mL/h. The constant flow was provided by a 2232 micropex peristaltic pump from Pharmacia LKB Biotechnology. The detection of the separated fractions was realised by a differential refractometer R401 (Waters Associates, The Netherlands). The samples were introduced by means of a sample applicator SA-5, delivered by Pharmacia LKB Biotechnology, used in a sample loop system. The eluted volumes were collected by a fraction collector TDC 220 from Gilson. For HFC fluids, 1-mL aliquots of 1 : 100 dilutions in water were injected on the system; for HFD U fluids, 1 mL of 2 : 100 dilutions in water/acetonitrile (80/20) were used.

### IR Identification of Polyalkylene Glycols

In the case of HFC fluids, any peaks eluting from the system and detected by the refractometer, were lyophilised in a Christ Alpha 1-4 lyophiliser. One and a half-milligram aliquots of each residue were mixed with 150 mg potassium bromide, pressed into a tablet and used to register the spectrum with a Perkin Elmer 197 infrared spectrometer.

In the case of HFD U fluids, the fractions collected were first heated in a water bath at 80°C using a stream of nitrogen in order to eliminate any acetonitrile present. Subsequently, the aqueous residues

were treated in the same way as the HFC fractions. The IR spectra of authentic standards (polyethylene glycol, polypropylene glycol, polyoxyethylene polypropylene glycol, ethylene glycol, propylene glycol) were recorded for comparison.

### NMR Identification

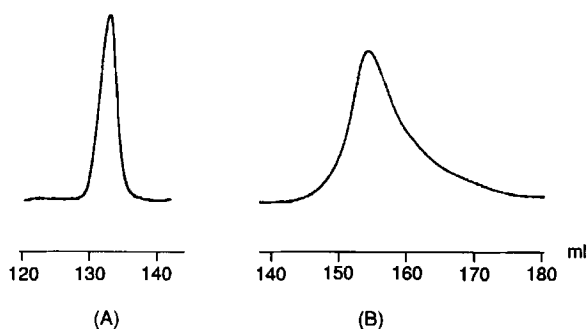
The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were obtained with a Jeol FX 90Q spectrometer (Tokyo, Japan). Tetramethylsilane was used as internal standard and  $\text{CD}_3\text{OD}$  as solvent (s, singlet; d, doublet; t, triplet; m, multiplet). The spectra were recorded on the industrial fluids and, when necessary, on selected fractions obtained from the GPC system. These fractions were first prepared as described for the IR study.

## RESULTS AND DISCUSSION

### Separation of Constituents and Molecular Weight Identification

The major objective of these experiments was to separate the different constituents of the HFC. Because precise information is lacking in the technical data sheets of many manufacturers, the separation efficiency of the system should be as high as possible. Five columns of two different types were tested, namely two Superdex columns and three Fractogel TSK columns.

The results demonstrate that adsorptions occur on Superdex columns. This is reflected by the observation of asymmetrical peaks and of elution volumes greater than the total volume of the packed bed in the case of Superdex 200 prep grade. Figure 1 shows the chromatograms of a polyethylene glycol standard with a mean molecular weight of 960, on

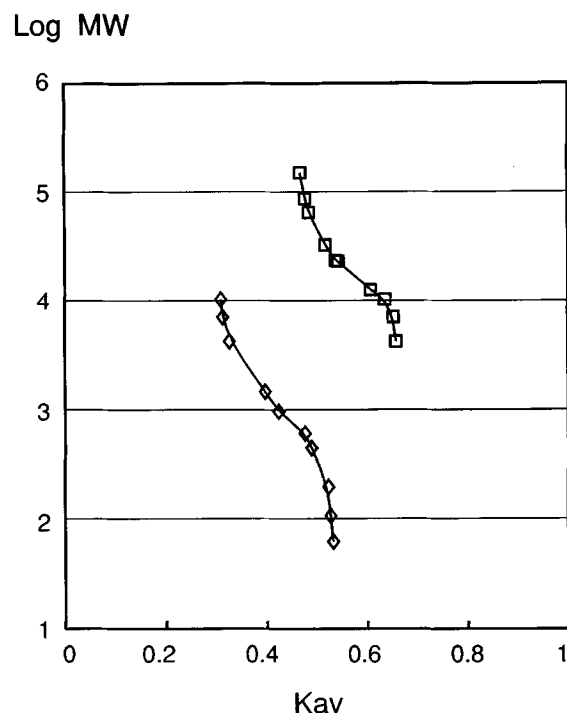


**Figure 1** Elution patterns of polyethylene glycol with mean  $M_w$  960 on (A) Fractogel TSK HW55(F) and (B) Superdex 200 prep grade.

(A) Fractogel TSK HW 55(F) and (B) Superdex 200 prep grade. Adsorptions on Superdex columns possibly may be the result of the natural origin of these gels, based on highly cross-linked porous agarose beads to which dextran has been covalently bonded. In order to eliminate these adsorptions on Superdex gels, other mobile phases have been studied. Better results were obtained with a mixture of water/acetonitrile (70/30). The introduction of a nonelectrolyte indicates that hydrophobic interactions were at the base of these adsorptions. However, with an increasing percentage of acetonitrile, the elution volumes decreased and adequate separations were not possible. This is reflected by the resolution calculations, shown in Table I and by the calibration curves on Superdex columns, shown in Figure 2.

**Table I** Specific Resolutions for Consecutive Pairs of Polyethylene Glycol on Two Superdex Columns

$M_w$	$\log M_w$	75 Prep Grade	200 Prep Grade
62	1.792		
		0.12	
106	2.025		
		0.27	
194	2.288		
		0.49	
440	2.643		
		1.37	
600	2.778		
		1.52	
960	2.982		
		1.14	
1470	3.167		
		0.69	
4250	3.628		
		0.43	0.33
7100	3.851		
			0.39
10300	4.013		
			0.77
12600	4.100		
			1.42
23000	4.361		
			1.78
23500	4.371		
			1.74
32500	4.512		
			1.63
64700	4.811		
			0.95
86500	4.937		
			0.48
150000	5.176		



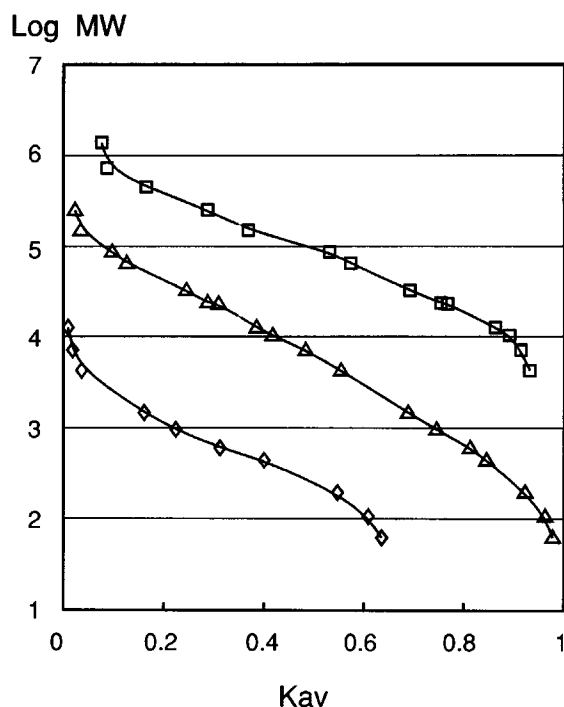
**Figure 2** Calibration curves for polyethylene glycol standards on ( $\diamond$ ) Superdex 75 prep grade and ( $\square$ ) Superdex 200 prep grade with water/acetonitrile (70/30) as eluents.

These specific resolutions ( $R_s$ ) were calculated between several pairs of polyethylene glycol standards using the following formula:

$$R_s = 2(V_2 - V_1)/(W_2 + W_1)(\log M_2 - \log M_1)$$

where  $V$ ,  $W$ , and  $M$  represent the elution volumes, peak widths at the base, and molecular weights, respectively, of two polyethylene glycols.<sup>3</sup>

On the contrary, separations on Fractogel columns, using bidistilled water as eluents were very satisfactory. Figure 3 shows the calibration curves of polyethylene glycols on different Fractogel TSK columns. The separation ranges corresponding to the linear part of the graphs are summarised in Table II. In order to evaluate separation efficiencies on Fractogel TSK gels, specific resolutions ( $R_s$ ) were calculated. In Figure 4, they are plotted against the average molecular weight of each of the two components on Fractogel columns. Although Fractogel TSK HW40(S) shows better resolution, Fractogel TSK HW55(F) is preferable because it allows the inclusion of polyalkylene glycols with a molecular weight higher than 4000. The latter are very often present as thickening agents in commercial hydraulic fluids.



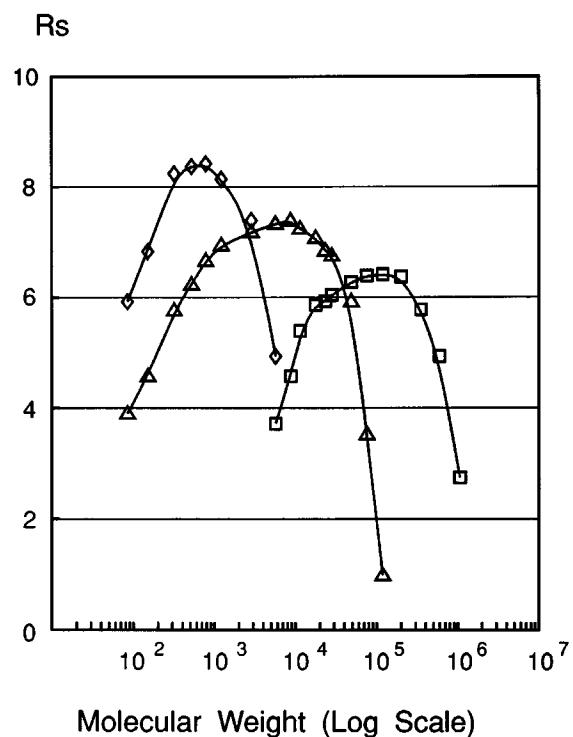
**Figure 3** Calibration curves for polyethylene glycols on ( $\diamond$ ) Fractogel TSK HW40(S), ( $\triangle$ ) Fractogel TSK HW55(F), and ( $\square$ ) Fractogel TSK HW65(F).

Recently, some new nonaqueous hydraulic fluids (HFD U) were introduced, also based on polyalkylene glycols. These mixtures have a very poor solubility in bidistilled water but are soluble in a mixture of bidistilled water and acetonitrile (80/20). This mixture was used as eluents on Fractogel TSK HW55(F). It was observed that the separation efficiency was lower than in the case of bidistilled water but still satisfactory. This is reflected by the greater slope of the calibration curve in comparison with the slope of that obtained with bidistilled water (Fig. 5).

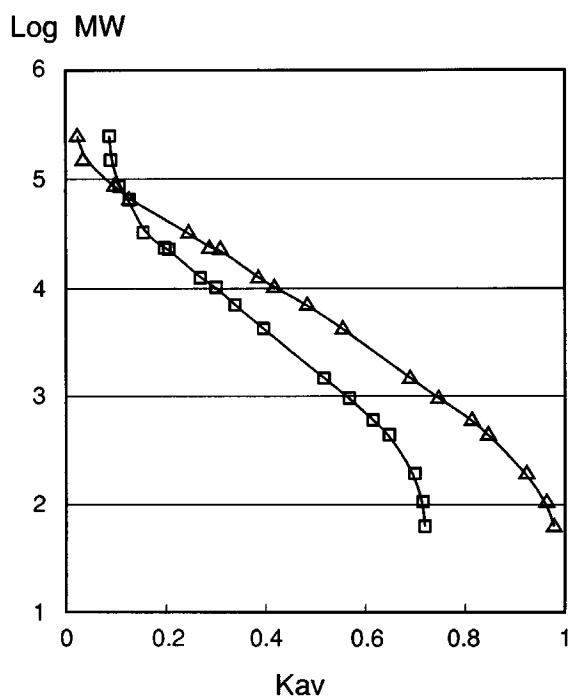
As shown in Table III, gel permeation chromatography permits the determination of the  $M_w$  of the different constituents present in HFC and HFD U fluids. This information, together with the  $M_w$  identification of decomposition compounds obtained during pyrolysis studies,<sup>1</sup> may contribute to the clarification of the decomposition pattern.

**Table II Separation Ranges for Polyethylene Glycols on Different Gel Types**

Gel Type	Separation Range
Fractogel TSK HW 40(S)	100–4000
Fractogel TSK HW 55(F)	200–75000
Fractogel TSK HW 65(F)	7000–600000



**Figure 4** Specific resolution plots against the average molecular weight on ( $\diamond$ ) Fractogel TSK HW40(S), ( $\triangle$ ) Fractogel TSK HW55(F), and ( $\square$ ) Fractogel TSK HW65(F).



**Figure 5** Calibration curves for polyethylene glycols on Fractogel TSK HW 55(F) with ( $\triangle$ ) bidistilled water as eluents and with ( $\square$ ) water/acetonitrile (80/20) as eluents.

**Table III** Molecular Weight Identification of Polymers Present in HFCs and HFD Us

Hydraulic Fluid	Type	Fraction	Molecular Weight
Glissosafe® 610	C	1	26937
		2	67
Glissosafe® 602	C	1	34728
		2	64
Glissosafe® V102	Thickener	1	35240
Pluracol® V10	Thickener	1	27132
Glykol I	Experimental	1	438
Glykol II	Experimental	1	694
Hydraulic TR 46	DU	1	865
Isocor E 46	DU	1	4749
		2	233
		3	71

### IR and NMR Spectroscopy

The following bands are seen in the IR spectrum of polyethylene glycol: 2870  $\text{cm}^{-1}$  (C—H stretching of  $\text{CH}_2$ , s); 1455  $\text{cm}^{-1}$  (C—H bending of  $\text{CH}_2$ , m); 1380  $\text{cm}^{-1}$  (C—H bending of  $\text{CH}_2$ , m); and 1105  $\text{cm}^{-1}$  (C—O stretch, s). For polypropylene glycol they are: 2970, 2940, 2880  $\text{cm}^{-1}$  (C—H stretch, m); 1460, 1375  $\text{cm}^{-1}$  (C—H bend, w); 1100 and 1015  $\text{cm}^{-1}$  (C—O stretch, m), of which the 2940 and 1015  $\text{cm}^{-1}$  bands are specific. The latter are also present in the copolymer of ethylene oxide and propylene oxide.

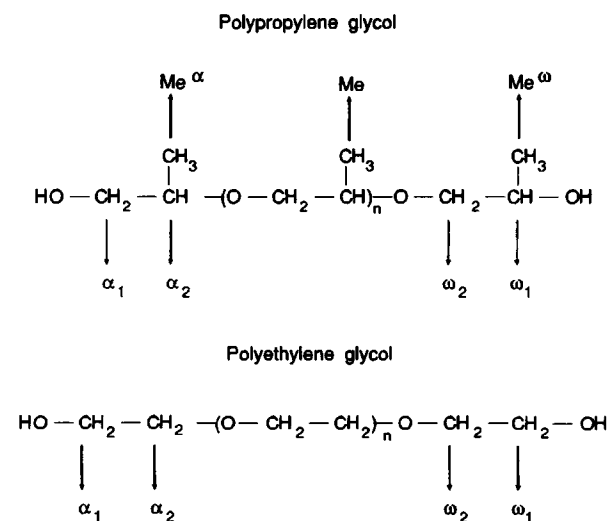
In the case of NMR, the conventions shown in Figure 6 are used. The  $^{13}\text{C}$  NMR shows the following  $\delta$  values for polyethylene glycol: 62.2 (C— $\alpha_1$ , C— $\omega_1$ ); 71.5 (C— $\beta$ ); and 73.6 (C— $\alpha_2$ , C— $\omega_2$ ). For polypropylene glycol  $\delta$  values are: 17.6 (Me); 19.6, 19.7 (Me $^\alpha$ , Me $^\omega$ ); 67.4 (C— $\alpha_1$ ); 67.9 (C— $\omega_1$ );

74.1–74.3 ( $\text{CH}_2$ ); 75.7 (C— $\omega_2$ ); 76.1 (C— $\alpha_2$ ); and 76.3–76.6 (CH).  $^1\text{H}$  NMR analysis ( $\text{CD}_3\text{OD}$ ) gave the following results for polyethylene glycol:  $\delta$  3.63 (s, —O— $\text{CH}_2$ — $\text{CH}_2$ —O—) and for polypropylene glycol:  $\delta$  1.1–1.2 (d, — $\text{CH}_3$ ); 3.4–3.6 (m,  $\text{CH}$ — $\text{CH}_3$ ); 3.4–3.5 (d, —O— $\text{CH}_2$ —). The spectra for other standards are known from commercial databases.

Table IV summarises the results for the different hydraulic fluids examined. It can be concluded that for HFC fluids the combination of gel filtration chromatography and IR spectroscopy makes it possible to verify the identity in a proper way. Glissosafe® 610 contains ethylene glycol and a copolymer of ethylene oxide and propylene oxide. Glissosafe® 602 contains ethylene glycol and polyethylene glycol. Glissosafe® V102 consists of polyethylene glycol and Pluracol® V10 of a copolymer of ethylene oxide and propylene oxide.

In the case of some HFD U fluids, a complementary NMR study is necessary. Indeed, contradictions are seen for some of them (Table IV). The infrared spectrum of Isocor® E46 does not show bands corresponding with a propoxy unit. The  $^1\text{H}$  NMR spectrum, however, shows the presence of the latter. Using the intensities of  $^1\text{H}$  NMR, an amount of approximately 3% propoxy can be estimated. When recording the IR spectrum of the separate fractions collected from the gel permeation chromatography (GPC) system, the propoxy unit could be assigned to propylene glycol, present as a minor fraction in the fluid.

The  $^{13}\text{C}$  NMR spectrum of the hydraulic TR46® fluid demonstrates additional peaks of low intensity with  $\delta$  values of 14.2 ( $\text{CH}_3$ ), 20.3 ( $\beta$ — $\text{CH}_2$ ), and 32.8 ( $\gamma$ — $\text{CH}_2$ ). These can be assigned to the presence of an extra butoxy unit in the copolymer. The ratio of that unit to the whole polymer is too low to permit its detection by IR spectroscopy.



**Figure 6** Nomenclature for polyethylene glycol and polypropylene glycol.

**Table IV Infrared and NMR Results for HFC and HFD U Fluids**

Hydraulic Fluid	Type	Spectrum of Mixture Corresponds With Standard of		Fractions Detected With	
		IR Spectroscopy	NMR Spectroscopy	Refractometer	IR Fractions
Glissosafe® 610	C	EO and PO	EO and PO	F1 F2	EO and PO EG
Glissosafe® 602	C	EO	EO	F1 F2	EO EG
Glissosafe® V102	Thickener	EO	EO	F1	EO
Pluracol® V10	Thickener	EO and PO	EO and PO	F1	EO and PO
Glykol I	Experimental	EO	EO	F1	EO
Glykol II	Experimental	EO and PO	EO and PO	F1	EO and PO
Hydraulic TR 46	DU	EO and PO	EO and PO	F1	EO and PO
Isocor E 46	DU	EO	EO and PO	F1 F2 F3	PG EO EO

EO, ethylene oxide units; PO, propylene oxide units; EG, ethylene glycol; PG, propylene glycol.

In the case of glykol II, additional problems occurred in dissolving this fluid. Even in a water/acetone mixture of 40/60, a nonsoluble fraction remains. The mixture was therefore split into an insoluble fraction, of which the IR was recorded, and into a soluble fraction that was submitted to the gel permeation system. The IR spectrum of the former fraction matches that of a copolymer of ethylene oxide and propylene oxide. Only one compound is seen in the soluble fraction after separation on GPC. The IR spectrum also indicates the presence of a copolymer spectrum of ethylene oxide and propylene oxide. However, the propoxy ratio is much lower than in the case of the insoluble fraction, as can be seen on the <sup>1</sup>H NMR spectrum.

## CONCLUSIONS

Although Superdex columns have superior separation efficiencies for dextrans and proteins, they are not suitable for aqueous gel filtration chromatography of HFC and HFD U fluids due to the small separation efficiencies. On the other hand, separation efficiencies on Fractogel TSK gels are very good. In the case of HFC fluids, the procedure with bidistilled water as eluents is preferable. A modified procedure is necessary to separate the different constituents of HFD U fluids due to the poor water solubility of the latter. Apart from the identification, the GPC method also allows the determination of the  $M_w$  of the polymers and monomers present in the industrial fluids.

The identity verification of HFC fluids could easily be realized by IR spectroscopy. In the case of

HFD U fluids, a complementary NMR study is indicated, due to a higher sensitivity of this technique. It is imperative to determine the identity of hydraulic fluids as precisely as possible to avoid underestimations of their probable toxicity.

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## REFERENCES

1. Commission of the European Communities—Safety and Health Commission for the Mining and Other Extractive Industries (Working Party on Rescue Arrangements, Mine Fires, and Underground Combustions). *Sixth Report on the Specifications and Testing Conditions Relating to Fire Resistant Fluids for Power Transmission in Mines*, 2786/8/SIE, Luxembourg, 1981.
2. A. R. Cooper and D. S. Van Derveer, *J. Liq. Chromatogr.*, **1**, 693 (1978).
3. Y. Kato, K. Komiya, H. Sasaki, and T. Hashimoto, *J. Chromatogr.*, **490**, 297–303 (1980).
4. Y. Kato, T. Matsuda, and T. Hashimoto, *J. Chromatogr.*, **332**, 39–46 (1985).
5. G. Callec, A. W. Anderson, and G. T. Tsao, *J. Polym. Sci.*, **22**, 287–293 (1984).
6. L. Kagedal, B. Engström, H. Ellegren, et al. *J. Chromatogr.*, **537**, 17–32 (1991).

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