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Qualitative Screening of Hazardous Waste Drum Mixtures

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■ Two automated infrared analysis techniques were reviewed as screening methods for unknown organic compounds in hazardous waste samples. The first method involves forward searching of spectra through a spectral library. The second method uses an automated artificial intelligence interpretation program named PAWMI. These two Fourier-transform infrared techniques were used on 11 hazardous waste samples that had been previously analyzed by gas chromatography/mass spectroscopy (GC/MS). The results of the forward searching showed that this method can be useful when the unknowns are relatively pure compounds and can be used to identify nonchromatographable components of mixtures. The PAWMI method demonstrated good success for those components of the waste present both in the program training set and in the samples at concentrations of >1%. This method should be used for on-site analysis of hazardous waste samples to identify major constituents of organic chemical mixtures in conjunction with compatibility testing and/or GC/MS analyses.

Introduction

During hazardous waste cleanup activities, a need exists to identify the major components of the waste mixtures. This information is useful in selecting worker and community protection programs, correctly determining which compounds can be bulked together, and helping identify appropriate disposal techniques (*1*). The two most common methods used to identify/classify hazardous wastes found in drums, tanks, and ponds are compatibility testing and gas chromatography/mass spectroscopy (GC/MS).

Compatibility testing is a group of basic qualitative methods that separates the waste into disposable categories. Because they can easily be performed on-site, the major advantages of compatibility testing procedures are their speed and relative low cost. The major disadvantage of compatibility testing is that the method separates unknown wastes into general categories (i.e., halogenated organic, acid, base, sulfide) but does not identify specific compounds (*1*). Also, compatibility testing screening procedures yield extremely limited results for mixtures of organic compounds. The most recent EPA-suggested method (*2*) for screening hazardous wastes for organic compounds involves a GC equipped with a flame ionization detector, using standards to identify possible compounds by comparing retention times. This method is semiqualitative at best.

GC/MS offers the ability to identify many volatile and semivolatile organic hazardous substances; however, recent findings (*2, 3*) have documented major compound classes in hazardous waste that are not detected by this method. In addition to chromatographic problems, other disadvantages of GC/MS as a waste screening tool on remedial action sites include high cost and time constraints (*1*). Although GC/MS has been performed on-site (*4*), samples are usually sent off-site to a laboratory when GC/MS analyses is required. This adds additional time and cost associated with preservation, shipping, and tracking the chain of custody of samples.

The emergence of Fourier-transform infrared (FT-IR) spectrometry has provided a method of sufficient sensitivity and rapidity for environmental analysis, especially as a method for the identification of major components of hazardous waste (*5–10*). FT-IR meets many of the requirements of a real-time screening technique for organic hazardous waste samples (*1*). Once the identity of the components of a complex mixture are known (*11–14*), FT-IR techniques can also be used to analyze the mixture quantitatively (*15*). Preliminary reports of its use in identifying components of hazardous waste samples suggest a promising role for this technique in the analysis of environmental samples (*5–10*). Interpretation techniques that can identify the components of a mixture have been reported (*16–22*).

An advantage of these techniques is the availability of search algorithms for the identification of pure compounds or commercial products. Most of these techniques employ forward-search algorithms where the unknown spectrum is compared to each member of the spectral database (*11–14*). These methods are successful for pure compounds, but they tend to fail when the compound is heavily contaminated by a second compound.

In this paper, we will demonstrate the use of two FT-IR methods to quickly identify major components of organic waste samples. The first method is forward searching the

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unknown spectrum against a library of known spectra of pure compounds, polymers, and commercial mixtures. The second method, PAWMI (Program for Automated Waste Mixture Interpretation), is an automated rule-based artificial intelligence program designed to identify the major components in the spectrum of a complex mixture (*23*). The method has been developed to identify 62 of the most commonly identified organic compounds on hazardous waste sites (*24, 25*).

Experimental Section

Forward searching and the PAWMI program, including rule writing, compiling, spectral generation, peak selection, spectral interpretation, and spectral similarity processing, were performed on a Nicolet 1280 computer equipped with a 160-megabyte storage module. This system was also used to acquire spectra from a 20-SX optical bench. Spectra were generated by use of two 13 × 2 mm KBr crystals with a background and sample signal averaging of 128 scans. The resolution was 2 cm^{-1}, which was obtained by collecting a 16 384-point interferogram and performing a 32 768-point transform.

Two infrared spectra were generated from each sample. The first spectrum was of the neat sample. The second spectrum was obtained of the sample after the KBr crystals were separated and the sample on the crystals was allowed to dry in the hood, at room temperature, for 10 min. By generating these two speectra and performing a computer subtraction of the dried sample from the neat sample, it was also possible to generate a third spectrum of the volatile fraction.

Forward Searching. The three spectra, generated from each of the 11 samples, were interpreted by the Nicolet forward-search routine (*13, 14*) against the Aldrich Neat Library of 4718 spectra of pure compounds and commercial mixtures. The 33 spectra were forward searched against the library with four different algorithms: absolute difference, least squares, absolute derivative, and square derivative (*13, 14*).

Program for Automated Waste Mixture Interpretation. PAWMI has three main subprograms: the interferogram processing and peak selection subprogram (PUSHSUB), the interpretation subprogram (Program for the Analysis of Infrared Spectra, or PAIRS), and final processing subprogram to subtract spectral similarity (PAIRSPLUS). The use of and effectiveness of PAWMI subroutines PUSHSUB and PAIRSPLUS are discussed in detail elswhere (*23, 26*). PUSHSUB selects peaks by transforming the first 256 data points right of the center burst from the original 16 384 data point sample interferogram into a threshold curve (low-resolution spectrum), which, when subtracted from the original sample, creates a spectrum with a straight base line for peak selection.

New rules were written for PAIRS that adapted it from a program that identifies fuctional groups of pure compounds (*27–33*) into a rule-based artificial intelligence program designed to identify the major components in an unknown mixture (*23*). The program uses peak location information and is based on a three-level filter algorithm designed to compensate for potential peak shifts in the mixture spectrum. If a peak falls in a relatively wide frequency window assigned to a certain compound, a percentage of the overall "goodness" value will be added to the total. Goodness is a measurement of closeness of match between the neat spectrum used in rule writing and the unknown spectrum. The goodness scale ranges from 0.01 for a total mismatch to 0.99 for a complete match. As the window size is reduced, the amount of goodness is increased for each level where the peak in the unknown spectrum still meets the criteria.

PAIRSPLUS was developed to limit the spectral similarity effect and thus increase the methods' ability to identify minor components in mixtures. PAIRSPLUS accesses both a data file for the spectral similarity that exists between the compounds in the training set and the interpretation results from PAIRS. The program then subtracts the percentage of spectral similarly corresponding to the compound with the largest goodness value from all the remaining compounds' goodness values. A check is then conducted on the remaining compounds to determine if another compound should be reported as present in the sample. If the next largest goodness value is greater than the upper limit of the 95% confidence interval, it is reported, the array is accessed, and the percentage of spectral similarity corresponding to its goodness value is subtracted from each remaining compound's goodness value. This is repeated until the statistical check determines there are no goodness values greater than the 95% confidence interval.

Hazardous Waste Samples. The 11 samples used in this study were obtained from the U.S. EPA National Enforcement Investigation Center (NEIC), in Denver, CO, and were collected from a midwest remedial action site. The only constraint placed on sample selection was that they were classified as an organic fraction during preanalysis compatibility testing. The viscosities of the samples ranged from free-flowing liquids to gelatinous solids. Analysis of the sample by GC/MS was conducted by EPA-NEIC. The samples were not refrigerated after the GC/MS analysis was performed.

The GC/MS analysis was performed with a Finnigan OWA on the methylene chloride extract for the extractable fraction of each sample and a Hewlett-Packard 5985 purge and trap/capillary GC/MS system for the volatile fraction. Standard methods specified by U.S. EPA protocols were used (*34*).

Results and Discussion

An area where the advatanges of qualitative FT-IR spectroscopy can be realized is direct identification of major components of mixtures. Direct identification techniques, by definition, require very little or no preseparation on the sample prior to spectral interpretation. This saves the time involved in chromatography and also has the advantage of enabling nonchromatographable compounds to be identified in the unknown waste.

Most FT-IR techniques utilize curve fitting or reverse-search algorithms to determine if a reference spectrum could be present in the mixture. However, these techniques frequently suffer from the basic assumption that the mixture can be constructed from a linear combination of the spectra of the pure components. This is rarely true because an IR spectrum is sensitive to the local environment of the molecules. Thus, the IR peak absorption maxima and width may be changed by the presence of other molecules in the sample being measured. These differences make the use of intensity information particularly difficult when looking for low-concentration components in the mixture.

In this experiment, samples were analyzed neat, then the samples were air-dried for 10 min in a fume hood, and the dried residue was reanalyzed. The spectra were subtracted to yield a difference spectrum representing the volatile fraction of the sample. These three spectra were then forward searched against the Aldrich Library with each of the four algorithms. It took a total of 90 s to search each of the spectra through the library by all four algorithms.

Table I. Results of GC/MS Analysis on Selected Hazardous Waste Samples

sample no.	compd[a]	%
1	ethyl acetate	46
	n-propyl acetate	17
	ethanol	7
	toluene	5
	butyl acetate	4
	methylcyclohexane*	2
3	xylenes	23
	cyclohexanone	17
	toluene	15
	4-methyl-2-pentanone	11
	ethylbenzene	10
8	*m*-cresol	14
	phenol	11
	dimethylphenol	8
	o-cresol	7
	2-ethylphenol	2

[a] Only compounds identified in concentrations greater than 1% are listed. * Compounds identified in hazardous waste samples by GC/MS that are not in the training set for PAWMI.

Following the forward search, the PAWMI program then interpreted the spectra of the neat sample and the volatile components. For each spectrum, PUSHSUB creates a file from which the mean absorbance is calculated, which is followed by peak selection and interpretation with PAIRS. The length of time required to carry out these manipulations and interpret a spectrum through the 62 rules (which are over 200 printed pages long) is 3 min.

Due to the amount of data generated in this study, only the results of analysis of three of the samples are discussed in detail for the forward search (samples 2, 3, and 7) and three samples in detail for the use of PAWMI (samples 1, 3, and 8). These examples were chosen because they most completely illustrate the factors involved in hazardous waste analysis. However, the results of the interpretation of all 11 samples were compiled and are briefly discussed.

Table I lists the results of the GC/MS analysis performed on samples 1, 3, and 8. Only compounds identified in concentrations greater than 1% are listed. As expected, all compounds found are volatile, and for each sample the total concentration is less than 100%. The reason that the results of the GC/MS analyses are used for the comparison with the results of the FT-IR analyses is that GC/MS is presently used as a benchmark for the analysis of hazardous waste samples (*1–5*). Thus, in almost all cases found in actual practice there are not data available other than GC/MS and compatibility testing data.

The training set of the PAWMI program is, at this point, based on an analysis of compounds that occur most frequently at hazardous waste remedial action sites (*24*). This training set is 62 compounds long. The compounds found in the three samples that are listed in Table I include some not in the training sett. These are marked with an asterisk. In the following discussion, results obtained with the PAWMI program are based only on compounds in the training set.

Forward-Search Results. Forward searching of the spectral library is most reliable when the unknown is a pure compound or commercial mixture. An approximation of this situation will exist for some hazardous waste samples after the volatile component is evaporated. The dried residue may then match a library spectrum. An illustration of this is shown in Figure 1, which shows the three spectra (neat sample, dried residue, difference spectrum representing the volatile components) generated from sample 3. The spectrum of the dried residue of sample 3 was

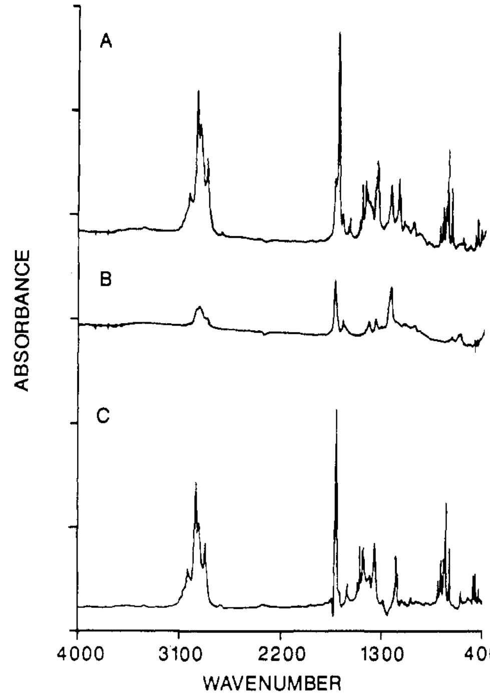

Figure 1. Three IR spectra generated from sample 3: neat (A), dried (B), and difference spectrum that represents the volatile fraction (A − B = C).

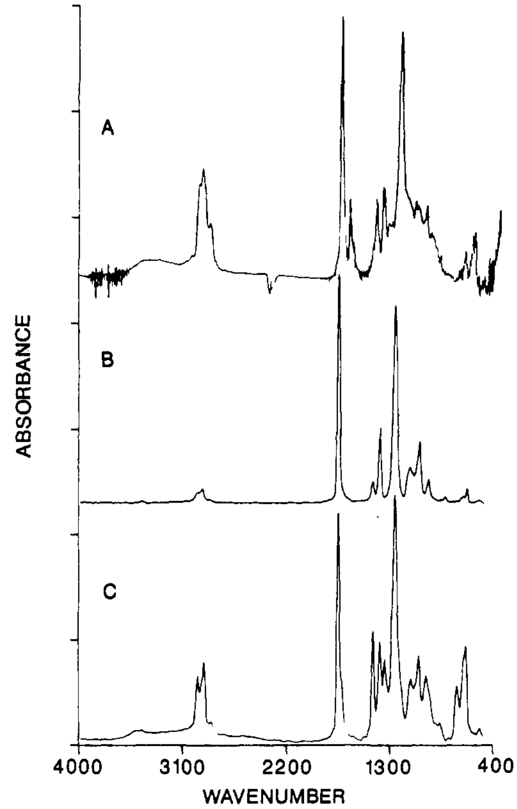

Figure 2. Comparison of spectrum of dried residue of sample 3 (A) and Aldrich Library closest matches poly(vinyl acetate) (B) and poly(vinyl acetate)/poly(vinyl chloride) copolymer (C).

identified by the absolute and square derivative algorithms as being poly(vinyl acetate) (PVA) or vinyl chloride/vinyl acetate copolymer (PVC/PVA), respectively. These spectra are shown in Figure 2 [(A) dried residue from sample 3; (B) PVA; (C) PVC/PVA copolymer].

Similar results are illustrated for the dried residues of sample 2 (Figure 3), identified as IGEPAL CA-720 nonionic surfactant [poly(ethylene glycol) *p*-nonylphenyl

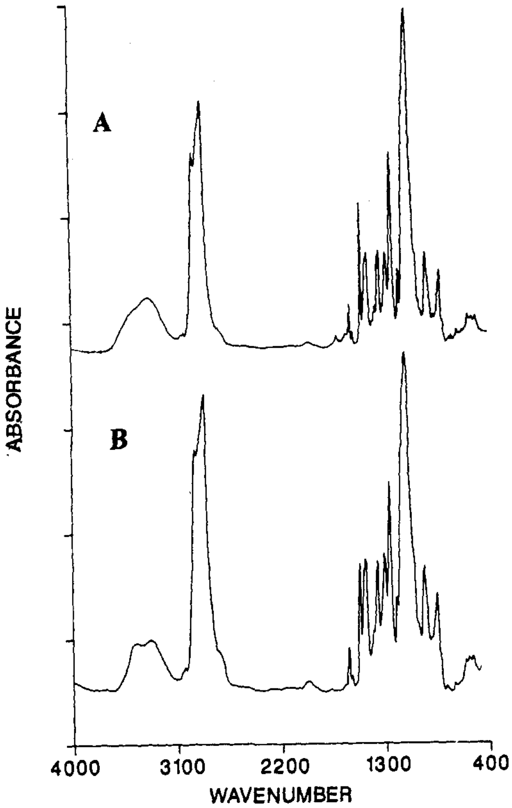

Figure 3. Comparison of spectrum of dried residue of sample 2 (A) and Aldrich Library closest match IGAPAL CA-720 (B).

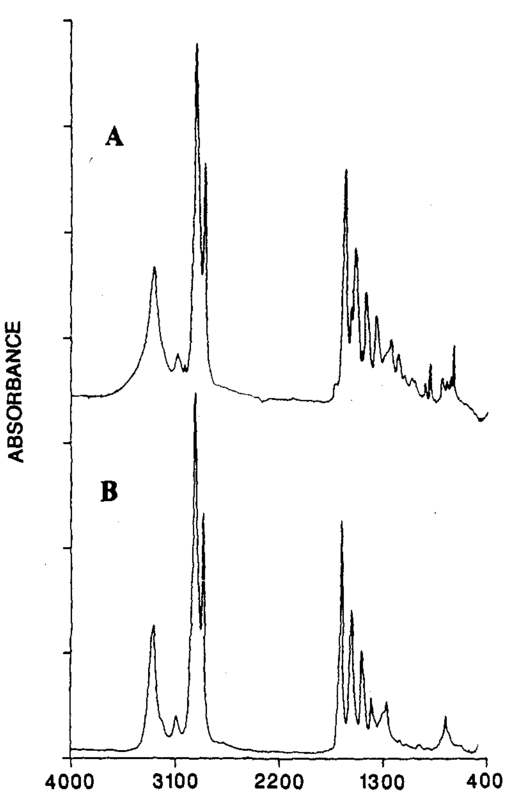

Figure 4. Comparison of dried spectrum of sample 7 (A) and Aldrich Library closest match polyamide resin (B).

ether], as matched by the square derivative algorithm. Similarly, close-match results are seen for sample 7 (Figure 4), identified as polyamide resin, as matched by the square derivative algorithm. Except for some slight contamination in the 800–1100 cm^{-1} region of the dried spectrum, the polyamide resin spectrum appears to be a perfect match.

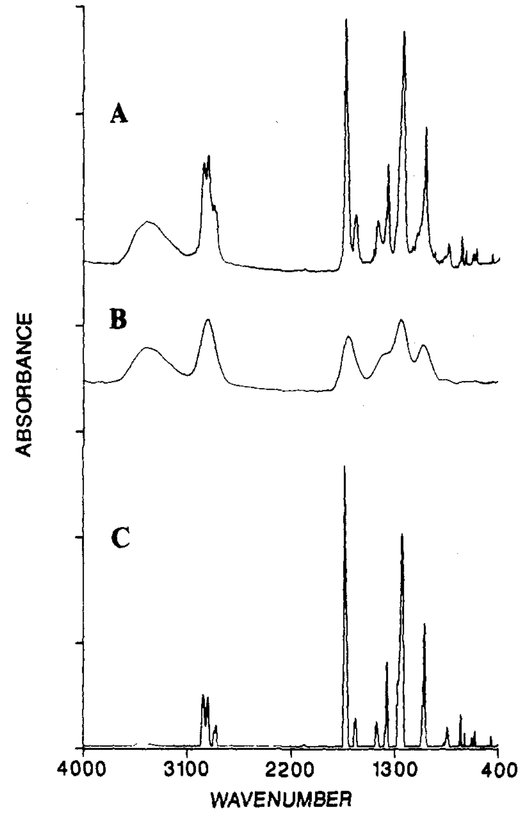

Figure 5. For sample 1, the neat spectrum (A), low-resolution spectrum (B), and results of the subtraction of the low-resolution spectrum from the high-resolution spectrum (C) are compared.

It is interesting to note that none of these species are identifiable by GC/MS techniques because they are nonvolatile polymers.

The best results obtained for matching the neat and volatile spectra to library spectra were obtained with the square derivative algorithm. This algorithm was able to correctly identify a major component of the waste spectra in 27% of the neat spectra and 55% of the subtract spectra. This is expected to improve substantially when the Aldrich Library is augmented by the availability of a library of paints, polymers, and related commercial products.

PAWMI. The process by which PAWMI interprets IR spectra begins with subtraction of the low-resolution spectrum from the high-resolution spectrum and the generation of a spectrum with a flat base line suitable for peak picking. This process is described in detail elsewhere (*23, 25*) and is illustrated in Figure 5. This process is applied to the neat and vapor spectra from each sample but not to the dried residue since the training set does not contain any polymers.

PAWMI can process both transmission and internal reflectance spectra. If a transmission spectrum is being processed, the threshold value is directly set to the mean absorbance of the data points in the subtracted file. If an internal reflectance spectrum is processed, a 1/wavelength correction (*35*) is applied to the spectrum before peak picking.

For the following discussions, a true positive is defined as a compound identified by PAWMI that was also found by GC/MS. A false positive is defined as a compound identified by PAWMI that was not found by GC/MS. A false negative is defined as a compound not identified by PAWMI that was identified by GC/MS, and a true negative is a compound not identified by either technique. Calculations of true and false negative results are made on the

Table II. Results of PAWMI Interpretation of Sample 1

sample type	PAIRS results: compd identified	PAIRS results: goodness value[a]	PAIRSPLUS results: compd identified
neat	*n*-butyl acetate	0.69	*n*-butyl acetate
	n-hexane[b]	0.68	toluene
	3-methylpentane[b]	0.64	*m*-ethyltoluene[b]
	n-propyl acetate	0.60	*n*-propyl acetate
	toluene[c]	0.52	1,1-dichloropropane[b]
			1-chlorodecane[b]
			ethyl acetate
			ethanol
volatile	*n*-propyl acetate	0.71	*n*-propyl acetate
			toluene
			ethyl acetate
			dibutyl phthalate[b]
			ethanol

[a] Only goodness values greater than 0.50 are listed. [b] False positive (for PAIRS analysis, compounds with goodness values greater than 0.59 that were not identified in the mixture by GC/MS; for PAIRSPLUS analysis, compounds identified that were not identified by GC/MS analysis). [c] False negative (for PAIRS analysis, compounds with goodness values less than 0.60 are considered not present in the mixture).

Table III. Results of PAWMI Interpretation of Sample 3

sample type	PAIRS results: compd identified	PAIRS results: goodness value[a]	PAIRSPLUS results: compd identified
neat	ethylbenzene	0.82	ethylbenzene
	4-methyl-2-pentanone	0.80	4-methyl-2-pentanone
	mixed xylenes	0.79	1,2-dichloropropane[b]
	n-butyl acetate[b]	0.77	toluene
	toluene	0.75	
	3-methylpentane[b]	0.70	
	n-hexane[b]	0.66	
	2-hexanone	0.59	
	n-propyl acetate	0.55	
	dibutyl phthalate	0.54	
	m-ethyltoluene	0.53	
volatile	toluene	0.72	toluene
	4-methyl-2-pentanone	0.70	4-methyl-2-pentanone
	ethylbenzene	0.62	mixed xylenes
	mixed xylenes[c]	0.59	2-hexanone[b]
	2-hexanone	0.57	
	n-butyl acetate	0.51	

[a] Only goodness values greater than 0.50 are listed. [b] False positive (for PAIRS analysis, compounds with goodness values greater than 0.59 that were not identified in the mixture by GC/MS; for PAIRSPLUS analysis, compounds identified that were not identified by GC/MS analysis). [c] False negative (for PAIRS analysis, compounds with goodness values less than 0.60 are considered not present in the mixture).

basis of compounds actually in the training set for PAWMI. For example, a compound not in the training set but found by GC/MS will not be counted as a false negative.

Sample 1. Table II lists the results of the PAWMI interpretation of the neat and volatile spectra of sample 1. By comparing the PAWMI results to the GC/MS results of sample 1 (Table I), it was determined that the PAIRS interpretation of the neat spectrum identified two true positives, 2 false positives, 3 false negatives, and 55 true negatives (remaining compounds in the training set that had goodness values less than 0.60). The PAIRSPLUS interpretation of the neat spectrum identified eight components in the mixture. Five of these were true positives (*n*-butyl acetate, toluene, *n*-propyl acetate, ethyl acetate, and ethanol), three were false positives (*m*-ethyltoluene, 1,1-dichloropropane, and 1-chlorodecane), zero were false negatives, and 54 were true negatives.

When the PAIRS interpretation was performed on the spectrum of the volatile fraction of sample 1, there was 1 true positive, 0 false positives, 4 false negatives, and 57 true negatives. The PAIRSPLUS interpretation of the volatile spectrum identified 4 true positives (*4*-propyl acetate, toluene, ethyl acetate, and ethanol), 1 false positive (dibutyl phthalate), 1 false negative (*n*-butyl acetate), and 56 true negatives.

For this sample, the PAIRSPLUS interpretation yielded more accurate results than the PAIRS interpretation. PAIRSPLUS identified all five major components of the neat waste for which rules were written. However, it also identified three false positives. The PAIRSPLUS interpretation of the volatile spectrum identified four of the five components of the mixture with only one false positive result. If the results obtained with PAIRSPLUS for both the neat and volatile sample spectra are considered together, it is found that four true positives and zero false positives have been identified.

Sample 3. Table III lists the results of the PAWMI interpretation of the neat and volatile spectra of sample 3. By comparing the PAWMI and GC/MS results (Table I), it was determined that the PAIRS interpretation of the neat spectrum identified 4 true positives, 3 false positives, 1 false negative, and 54 true negatives. The PAIRSPLUS interpreation of the neat spectrum identified four components in the mixture, three of which were true positives. One compound identified was a false positive, and there were 2 false negatives and 56 true negatives.

When the PAIRS interpretation was performed on the spectrum of the volatile fraction of sample 3, there were 3 true positives, 0 false positives, 2 false negatives, and 57 true negatives. The PAIRSPLUS interpretation of the volatile spectrum identified 3 true positives, 1 false positive, 2 false negatives, and 56 true negatives.

For this sample, the PAIRS interpretation identified more true positives than the PAIRSPLUS interpretation. The reason for this is the spectral similarity between three of the components of the mixture (toluene, ethylbenzene, and xylene). Because these compounds are very similar, their infrared spectra are very similar; thus, the rules used to identify them in mixtures are similar. Therefore, it is probable that when a large goodness value is returned by the interpreter for one of them, substantial goodness values (greater than 0.60) may be returned for the others. This will be true if the spectrally similar compounds are in the mixtures or not. PAIRSPLUS subtracts this spectral similarity information from the PAIRS results to identify minor components of mixtures. However, in this case, because the spectral similarity is so great, it eliminates one of the true positives in each of the PAIRSPLUS interpretations. Note that in Table III the PAIRSPLUS results of the neat spectrum identify ethylbenzene and toluene but not mixed xylenes, even though it had a goodness value of 0.79 during PAIRS interpretation. The results of the PAIRSPLUS interpretation of the volatile spectrum identify toluene and mixed xylenes but missed ethylbenzene. A more detailed study of PAWMI's ability to identify minor components in mixtures is given elsewhere (*23, 26*).

Sample 8. Table IV lists the results of the PAWMI interpretation of the neat and volatile spectra of sample 8. By comparing the PAWMI results to the GC/MS results of sample 8 (Table I), it was determined that the PAIRS interpretation of the neat spectrum identified 1 true positive, 0 false positives, 4 false negatives, and 57 true negatives. The PAIRSPLUS interpretation of the neat spectrum identified five components in the mixture. All five of these were true positives (phenol, *m*-cresol, 2-ethylphenol, *p*-

Table IV. Results of PAWMI Interpretation of Sample 8

sample type	PAIRS results: compd identified	PAIRS results: goodness value[a]	PAIRSPLUS results: compd identified
neat	phenol	0.70	phenol
	p-cresol[b]	0.52	*m*-cresol
	m-cresol[b]	0.52	2-ethylphenol
			p-cresol
			dimethylphenol
volatile	phenol	0.80	phenol
			n-hexane[c]
			2-ethylphenol
			1,1-dichloropropane[c]
			dimethylphenol

[a] Only goodness values greater than 0.50 are listed. [b] False positive (for PAIRS analysis, compounds with goodness values greater than 0.59 that were not identified in the mixture by GC/MS; for PAIRSPLUS analysis, compounds identified that were not identified by GC/MS analysis). [c] False negative (for PAIRS analysis, compounds with goodness values less than 0.60 are considered not present in the mixture).

Table V. Review of PAWMI's Ability To Identify Major Components of Eleven Hazardous Waste Samples

	PAIRS		PAIRSPLUS	
	neat	volatile	neat	volatile
true positives	17	16	29	27
false positives	7	5	11	11
percent false positives	29	24	28	29
false negatives	22	23	11	12
true negatives	635	638	631	632
total	682	682	682	682
positives (IR/GC-MS), %	44	41	74	69
negatives (IR/GC-MS), %	98.9	99.2	98.3	98.3

cresol, dimethylphenol). There were 0 false positives, 0 false negatives, and 57 true negatives reported.

When the PAIRS interpretation was performed on the volatile spectrum of sample 8, there was 1 true positive (phenol), 0 false positives, 4 false negatives, and 57 true negatives. The PAIRSPLUS interpretation of the volatile spectrum identified 3 true positives (phenol, 2-ethylphenol, and dimethylphenol), 2 false positives (*n*-hexane and 1,1-dichloropropane), 2 false negatives (*m*-cresol and *o*-cresol), and 55 true negatives.

The PAIRSPLUS interpretation was superior to PAIRS for this sample. The PAIRS interpretation of the neat spectrum identified one component of the mixture while the PAIRSPLUS interpretation of the neat spectrum identified all five of the components, with zero false positives and negatives.

Table V reviews PAWMI's ability to identify major components of waste mixtures by direct interpretation of the infrared spectra of the neat waste mixture and the volatile fraction of the waste, for those components at or above the 1% concentration level. The percentage of compounds in the IR training set rules and identified by the FT-IR interpretation technique, and also identified by GC/MS, was 41–44%. This improved to 69–74% for PAIRSPLUS interpretations. This means that by use of the PAIRSPLUS interpretation on the neat spectra, approximately 70% of the compounds in the mixtures, at concentrations greater than 1%, which were in the training set, were identified.

The percentage of compounds that are in the training set and not identified by the FT-IR interpretation techniques, and also not identified by GC/MS, was 99% for PAIRS and 98% for PAIRSPLUS. Thus, by performing PAIRSPLUS interpretation of the PAIRS results, the number of true positives is increased, but the number of false positives is also increased.

Conclusions

Two FT-IR techniques were used to identify major components of 11 previously analyzed hazardous waste samples, using direct-mixture interpretation techniques. The results of the forward searching showed that this technique can be a strong tool when the unknowns are relatively pure compounds or commercial mixtures with library spectra that are available. Forward searching was shown to have the ability to identify nonchromatographable components of the mixtures, which could not be determined by standard GC/MS. Forward searching should show improved results with the addition of an extended library of polymers and paint components. The second method, PAWMI, was shown to have good success in identifying components of mixtures that were in concentrations greater than 1%.

With the reliability of the FT-IR hardware, the lack of sample preparation, and the speed of these two interpretation techniques, FT-IR has become an additional screening method for unknown organic hazardous waste mixtures. This technique can offer chemical information beyond compatibility testing procedures and can identify components that could not be identified by GC/MS. This method is not a trace analysis technique and should be used for analysis of hazardous waste samples at a hazardous waste remedial action or licensed disposal site to identify major constituents of organic chemical mixtures in conjunction with compatibility testing and/or GC/MS analyses.

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Registry No. Ethyl acetate, 141-78-6; *n*-propyl acetate, 109-60-4; ethanol, 64-17-5; toluene, 108-88-3; butyl acetate, 123-86-4; methylcyclohexane, 108-87-2; xylene, 1330-20-7; cyclohexanone, 108-94-1; 4-methyl-2-pentanone, 108-10-1; ethylbenzene, 100-41-4; *m*-cresol, 108-39-4; phenol, 108-95-2; dimethylphenol, 1300-71-6; *o*-cresol, 95-48-7; 2-ethylphenol, 90-00-6; *n*-hexane, 110-54-3; 3-methylpentane, 96-14-0; 2-hexanone, 591-78-6; dibutyl phthalate, 84-74-2; *m*-ethyltoluene, 620-14-4; *p*-cresol, 106-44-5.

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Contamination of Soil around Wood-Preserving Facilities by Polychlorinated Aromatic Compounds

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■ The fate of the different constituents of wood-preserving chlorophenol formulation in soil near the preserving facilities at four different sawmills was studied. The sawmills were in normal operation during the examination period. Penetration and stability of chlorophenols and the dimeric impurities of the contaminating formulation polychlorinated phenoxyphenols and polychlorinated dibenzofurans in soil were followed. The concentrations of all compounds were very high in soil, 500–3500 ppm for chlorophenols, 1–50 ppm for polychlorinated phenoxyphenols, and 0.2–5 ppm for polychlorinated dibenzofurans (dry weight of soil), showing that soil was heavily contaminated near the preserving facilities. No clear decrease of soil concentrations of these compounds was seen within 1 year after one mill stopped using technical chlorophenol. Chlorophenols were found to be metabolizable and mobile in soil whereas polychlorinated phenoxyphenols and polychlorinated dibenzofurans were persistent and immobilized in the top layer of the soil.

Introduction

Technical chlorophenol (CP, Figure 1) formulations have been widely used as preservatives against rot and bluestaining of wood by fungi in the sawmilling industry both in Europe and in the U.S.A. CPs are toxic for terrestial and aquatic life. The use of technical CPs has led to serious pollution of the environment and hazardous situations at the work place (*1–8*). Commerical CP formulations are usually synthesized by direct chlorination of phenol yielding a mixture of CPs, the main components being pentachlorophenol (PCP), 2,3,4,6-tetrachlorophenol (TeCP), and 2,4,6-trichlorophenol (TCP), and the byproducts polychlorinated phenoxyphenols (PCPPs, Figure 1) (*9–11*), polychlorinated diphenyl ethers (PCDPEs) (*11, 12*), polychlorinated dibenzofurans (PCDFs, Figure 1) (*11, 12*), and polychlorinated dibenzodioxins (PCDDs) (*11–13*). It was for reasons of the toxicity of the active ingredients and these impurities that Sweden banned the use of CPs for wood preservation in 1978, and the U.S. EPA has recently issued a ban, effective since 1984 (*14*), on consumer market use of PCP. In Finland, the manufacture of CPs-containing wood preservative for sawmill use was discontinued in 1984.

There are many reports on the wide-spread contamination of the environment caused by leaching of CPs from dumping sites (*15, 16*) or following accidental spill of CPs from industries using these chemicals (*1, 3, 17*). We have earlier shown that normal operation of a CP dip-treatment facility for timber and lumber in the sawmill industry has lead to serious local contamination of soil and groundwater (*18, 19*) by CPs and the minor constituents of technical CP formulations, PCPPs (*10, 11, 19*) and PCDFs (*11*). This work was done to measure the leachability, vertical migration, and persistence of these compounds in soil.

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