



Project Summary

Collection and Interpretation of Level 1 IR and LRMS Data

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Approaches to measurement and interpretation of infrared (IR) and low resolution mass spectra (LRMS), taken by four Environmental Protection Agency (EPA) contractors following the guidelines of the Level 1 Environmental Assessment Program, were evaluated. The mechanism of evaluation involved supplying each contractor with test spectra, and samples for analysis and interpretation. Using IR, the contractors identified 55-85% of the structural moieties present in the various samples or indicated by the various test spectra, with 85% being approximately the maximum attainable. Sources of error in IR measurement included analyst-to-analyst variation in signal location of $\pm 5-10 \text{ cm}^{-1}$ and failure to optimize signal intensity through proper loading of the salt plates or KBr pellets. IR interpretation errors disclosed were errors of omission and assignment. To improve IR data quality, all significant signals must be interpreted, including those complementary signals that support or refute other assignments; also, reasonable, alternative interpretations must be considered. The contractors identified 50-90% of the compound classes represented using LRMS. LRMS interpretation errors disclosed were failure to find molecular ions, reporting molecular ions as fragment ions and vice versa, incorrectly identifying molecular ions and incorrectly assigning ions to homologous series. To improve LRMS data quality, the refer-

ence series *Eight Peak Index of Mass Spectra*, Imperial Chemical Industry, Ltd., 1970, First Edition, Mass Spectrometry Data Center, Alder Maston, Reading, United Kingdom, should be used, intensity and mass/charge range criteria set to simplify spectra, the LC fraction data used with caution, and IR and LRMS data analyzed independently to avoid bias.

Objective of the Study

Infrared (IR) spectrometry and low resolution mass spectrometry (LRMS) are two of the principal methods used in the Level 1 program for semiquantitative determination of organic classes and compounds. These methods have proven suitable for this task in a variety of successful Level 1 studies. It appears, however, from several evaluations of the Level 1 program, that these techniques are not always being used by environmental assessment contractors to maximize the output of useful data from Level 1 LC fractions 4, 5, and 6. This problem could arise from a number of sources; for example, poor sample preparation, poor instrumental techniques, or weakness in spectral interpretation. One objective of the study described herein has been to identify these sources of difficulty and to suggest ways to overcome or reduce their magnitude. A second objective has been to identify the positive components of the contractors' use of these techniques that lead to high quality results.

Approaches to Investigation

There were two stages in this study. In the first stage, six IR and six LRMS test spectra were prepared using samples that varied in both complexity and variety of organic functional group content. The spectra were acquired using six samples blended to represent Level 1 LC fractions 4, 5, and 6. There were two different samples for each of the three LC fractions and the spectra were prepared following Level 1 procedures. These spectra were sent to four contractors selected by the EPA Project Officer (Arthur D. Little, Inc., Battelle Columbus Laboratories, Southern Research Institute, and TRW Systems.

The contractors were requested to interpret the spectra as normal Level 1 spectra. A copy of the organic analysis chapter of the Level 1 Environmental Assessment Manual (Second Edition, Lentzen et al., EPA-600/7-78-201) was provided for guidance in this task. No special efforts were to be made with these spectra beyond that expected for Level 1 work. However, the contractors were asked to clearly indicate the spectral characteristics leading to the identification of functional groups, structural characteristics, or, when possible, individual compounds or compound classes. Using the analysis sheets provided, the contractors were to spell out clearly the reasoning behind each assignment, including information about peak wavelength or mass, peak magnitude or shape, patterns of peaks, or correlation with LC fraction number. Also, if the LRMS data proved useful to the IR interpretation and/or vice versa, the contractor was to state this fact and explain.

The returned test results were studied with respect to accuracy, thoroughness of interpretation, approach to interpretation, etc. On the basis of these results, two synthetic samples were prepared and sent to the contractors for both IR and LRMS analysis. The samples for this second stage of the investigation were prepared to represent LC fractions 5 and 6. They were prepared principally from compounds that were used to prepare the stage one spectra and that had proved difficult to identify previously. This was done, in part, to determine if measurement of their own spectra would improve the contractors' abilities to make accurate analyses as well as to test the residual problems identified with the stage one spectra. Included

with the two synthetic samples, was a sample of tar from a coal gasification unit. This sample was to be separated using the Level 1 LC scheme, and fractions 4, 5, and 6 were to be analyzed using IR and LRMS. The contractors were also given the option of analyzing other fractions and reporting these results if they felt such data would be useful in interpreting the results from 4, 5, and 6.

The spectra and interpretation results from this second state of the study were returned and have been studied in conjunction with the earlier interpretation results with regard to accuracy and sources of error. Approaches to spectral interpretation have also been investigated through personal visits and/or telephone conversations with the contractor spectroscopists. Wherever possible, the interpretation based on LRMS was separated from that aided by IR and vice versa. The results of these investigations and studies are presented in detail in the project final report. They are summarized here, and recommendations for improvement of the IR/LRMS techniques, as used in Level 1 environmental assessment, are presented.

IR Studies

The results of the contractors' measurement and interpretation efforts were generally acceptable. Accuracy of identification of functional groups and other structural moieties indicated by the synthetic spectra, the spectra from the synthetic samples, and spectra from the tar samples are shown in Table 1.

Table 1. Accuracy of Functional Group/Structure Identification Using IR (%)

	Contractor			
	A	B	C	D
Test Spectra	85	65	85	60
Test Samples	55	55	80	80
Tar Samples	80	70	65	85

An accuracy level of 80% is considered very acceptable; in general, identification at this accuracy level means that only the structures most difficult to identify have been missed. Contractors A and C achieved less than 80% accuracy levels on two sample types principally because of low-quality spectral data. Contractors B and D

achieved low levels principally because of inaccurate and incomplete spectral interpretations.

IR Measurements

In addition to interpreting the six spectra provided, the contractors made IR measurements with three samples—two synthetic mixtures and a sample of coal tar. Three components of the measurement process were observed to have a significant effect upon the final interpretation results:

1. Variation in band location from contractor to contractor for bands from the same structural source;
2. Signal intensity not optimized; and
3. Weakness or absence of bands in the 4000-2000 cm^{-1} range in spectra obtained with KBr pellets.

The variation in band location was in the range of $\pm 5 - \pm 10 \text{ cm}^{-1}$. This variation was due both to variation in the actual locations of the bands in the spectra and also to inexact assignment of the band locations by the analyst.

Signal intensity cannot always be optimized because of insufficient sample quantity; however, overloading of the salt plate or KBr pellet, which can and must be controlled, was observed and had the effect of weak or medium signals being falsely identified as medium or strong signals.

The most serious of the three factors observed was the weakness or absence of signals in the 4000-2000 cm^{-1} range in spectra obtained with KBr pellets as compared to those obtained with salt plates. This weakness or absence may be a result of interaction with the KBr, energy loss due to cloudy pellets, or a loss of volatile compounds which occurs during preparation of the KBr pellets. For example, the two contractors using KBr pellets missed aliphatic CH in the 3000-2900 cm^{-1} range apparently because of insufficient signal; the two using salt plates did have signals attributable to aliphatic CH in this range.

IR Interpretation

Several types of errors were observed to affect the levels of accuracy of identification achieved. These include failure to interpret bands, simple assignment errors, assignments made that were rational but not correct, and failure to use alternate bands to support or dispute assignments based on other bands.

Bands Not Used—Both primary and secondary bands for structural or functional groups were not used. Examples of data not used are presented in Table 2.

Errors in Assignment—Examples of errors in assignment, which were not often made, are shown in Table 3.

Rational, Though Incorrect, Assignments—Rational, though incorrect, assignments arise because different structures and functional groups give rise to bands in the same wavelength regions. Examples of these errors are given in Table 4.

Incomplete Use of Available Information—Most structures give rise to several bands that have regular relationships in terms of wavelength, magnitude, and breadth. Such complementary bands serve both to support and dispute assignments. Examples of such complementary data not used are:

1. A band at 1240 cm^{-1} is described as being due to an ester. There is no band at 1735 cm^{-1} ($\text{C}=\text{O}$), however, which refutes the 1240 cm^{-1} assignment.
2. A band at 1240 cm^{-1} is described as being due to C-O of ether. Another band at 1015 cm^{-1} , which is apparently due to symmetric stretch of C-O-C and which supports the 1240 cm^{-1} assignment, was not utilized.
3. A band at 1590 cm^{-1} is described as being due to an amine. This band location is typical of a primary amine, which was not indicated. Bands at 1180 cm^{-1} and 1235 cm^{-1} , which could be the C-N stretch of a primary amine and which support the 1590 cm^{-1} assignment were not utilized.

Other Factors Affecting Accuracy of Identification

Spectroscopist Experience—There was a correlation between accuracy of interpretation and experience of the spectroscopists, though this correlation was weak. The accuracy levels attained by spectroscopists with 25 years, 22 years, 11 years, 7 years, 3 years, and 6 months experience (one contractor had three spectroscopists involved in the study) were in the relative order 1, 3, 4, 2, 6, and 5, respectively.

Table 2. Selected Examples of Unassigned Bands Found in Various Spectra

Band not assigned, cm^{-1}	RTI assignment
2930, 2850	Saturated CH
1680, 1670	Carbonyl
1430, 1240	Coupling of acid OH/C-O groups
1450, 1465, 1390, 1380, 1364	CH_3
1240, 1160, 1100	C-O of alcohol

Table 3. Selected Examples of Errors in Assignment of Bands

Band, cm^{-1}	Apparently erroneous assignment	Apparently correct assignment
1850	Carbonyl	Overtone or summation band
1600	Unsaturated CH	Aromatic C=C
1480, 1470	Unsaturated CH	CH_3
1510	C-N	Aromatic C=C
3052	OH	Unsaturated CH

Table 4. Selected Examples of Rational, Though Incorrect, Assignments

Band, cm^{-1}	Apparently erroneous assignment	Apparently correct assignment
1715, 1690	Carbonyl	Overtone or summation bands
1710	C=O of ester	C=O of ketone
1280, 1240	C-O of aromatic alcohol	CH_3
1235	C-O of aromatic alcohol	C-N of carbazole
1300	C-N of aryl amine	OH/C-O coupling

Time Given to Interpretation—The time given to interpretation of the spectra dealt with in this study ranged from 1-4 hours per spectrum, though the 4 hours included time for assignment of all IR bands to compounds already identified by LRMS. No strong correlation between accuracy of interpretation and time given to interpretation was found.

Disagreement Among Standard Sources of Band Information—Various reference works produced by experts show disagreement regarding band assignments as is illustrated in Table 5. This variation does not lead to very many errors because the spectroscopists apparently rely more on their

experience than on reference works of this sort. It has been proposed that a written guide for interpretation be prepared, which includes an assignment table for wavelength correlation with compound category. PMB-IERL/EPA is, in fact, considering preparation of such a document.

Approaches to Interpretation—The approaches to interpretation taken by the spectroscopists are generally similar. Major bands are assigned as probably being due to certain functional or structural groups. Secondary bands are then examined, with reference works being used in this latter stage. Pattern recognition is important to some of the spectroscopists.

Table 5. Wavelength Ranges Indicated for Different Structures as Found in Three Different Reference Sources

Structure	Reference Source		
	<i>N. B. Colthup (1950)</i>	<i>Dow Chemical</i>	<i>Nakanishi (1962)</i>
<i>C-O stretch of alcohol</i>	1290-1000 cm^{-1}	1260-980 cm^{-1}	1200-1000 cm^{-1}
<i>NH bend of primary amine</i>	1640-1560 cm^{-1}	1665-1625 cm^{-1}	1640-1560 cm^{-1}
<i>Aromatic C=C</i>	1650-1550 cm^{-1} 1540-1450 cm^{-1}	1665-1615 cm^{-1} 1515-1370 cm^{-1}	1600-1450 cm^{-1} -
<i>C-O-C of aliphatic ether</i>	1175-1055 cm^{-1}	1140-1090 cm^{-1}	1200-1040 cm^{-1}

IR—Conclusions and Recommendations

In the area of IR measurements, two significant sources of error have been observed. First, the concentration of the test sample must be optimized if at all possible. Too few samples result in signals being missed and too many samples result in signal intensities being assigned incorrectly. Second, it appears that spectra acquired with KBr pellets are of relatively poor quality in the 4000-2000 cm^{-1} range compared with those acquired with salt plates. It is premature, however, to recommend that only salt plates be used because the data base is limited, and these apparent sources of error should be investigated further.

Some of the errors observed arise from problems in measurement. Most arise, however, from errors in interpretation. Errors in interpretation are apparently due to unintentional oversights, incorrect information about the location of bands due to certain structures, and/or prior experiences with certain structures or compounds that have proven misleading. Such errors are best eliminated by having the spectroscopist occasionally verify his or her interpretations through the use of reference materials and/or having interpretation results occasionally checked or audited by a second, outside spectroscopist, or providing Level 1 and other EPA contractors with standard assignment charts and instructional courses. Other errors are the result of bias on the part of the spectroscopist, not using other bands in the spectra which would support or dispute the interpretation of the band in question, and/or not considering all reasonable

interpretations of the bands in a spectrum.

These last two reasons for errors are related to a general interpretation problem—not using all available information in a spectrum. Most structures give rise to several bands in a spectrum and all should be considered when one is trying to defend or refute the presence of a particular structure. In some cases, a lone band or a group of bands will indicate two or more possible structures. All reasonable interpretations should be presented, with, if possible, some estimate of the relative amounts of these structures. One should not, however, carry this process too far and report every possible functional group for a given peak maxima. The presence or absence of confirmatory bands should dictate the final assignment(s).

The quality of the results presented by each spectroscopist is, in general, a reflection of his or her level of experience and the time given to interpretation of each spectrum, though the correlation is not strong. In fact, it is the thoroughness of the interpretation that seems to have the greatest bearing on the quality of the results. A thorough interpretation requires, however, that the spectroscopist consider all possible (and reasonable) structures that could be present in a sample. This means that the spectroscopist must have thorough training and/or a great deal of experience. Alternatively, he or she must make extensive use of reference materials. In either case, thoroughness may be expensive in terms of dollars and hours. Such thoroughness may also present a problem as the work load in the environmental assessment area increases. To deal with both the need for

thoroughness in interpretation and the increased work load, some sort of computer assistance for the spectroscopist should be considered.

LRMS Studies

LRMS Measurements

The contractors obtained low resolution mass spectra on three samples—two synthetic mixtures blended to represent Level 1 LC fractions 5 and 6, and a sample of coal tar. All samples were analyzed using a direct insertion heated probe with a series of spectra taken on a sample as the sample was being volatilized from the probe. Three out of four analysts obtained their spectra via digital readout recording systems. One analyst obtained the spectra via an analog oscillographic trace.

No differences in the quality of the spectral data obtained or in the results of the contractor's analyses of these data were found to be attributable to the instrumentation or measurement techniques used. For example, although one contractor found that spectra taken at low (15 eV) ionizing voltage was useful in the identification of molecular ions not easily disclosed from the 70 eV spectra, the other contractors did not use this approach, nor did it appear to significantly affect the overall quality of results for these three samples.

LRMS Interpretation

In evaluating the results, it was soon apparent that very often a category assignment was based on the assignment of peaks to one compound. Nevertheless, the primary goal of Level 1 environmental assessment is the identification of compound classes. Thus, for the purposes of this study, correct compound class identification is given greater significance than the identification of individual compounds, although this information is also very important.

The results of both stages of the spectral interpretation test indicated that 50-90% of the compound classes present in the eight synthetic mixtures were correctly identified (Tables 6 and 7). The categories most often missed were fused ring acids, ketones, and phenols. Many individual compounds were also identified by the contractors in the test spectra (Table 8) and test samples (Table 9).

Table 6. Categories in the IR/LRMS Spectral Interpretation Test Correctly Identified by LRMS (Sum of Intensities of Compounds in the Categories)

Category	mg/L	Weight %	Contractor			
			A	B	C	D
LC4a Fused alternate, nonalternate hydrocarbons	15,835	100.0	810	*	630	320
LC4b Fused alternate, nonalternate hydrocarbons	16,813	100.0	260	*	280	321
LC5a Fused alternate, nonalternate hydrocarbons	3,016	14.0	NR	NR	20	NR
Heterocyclic nitrogen compounds	18,584	86.0	130	*	330	231
LC5b Heterocyclic nitrogen compounds	12,105	92.2	210	*	340	110
Ketones	1,016	7.7	110	*	10	111
LC6a Heterocyclic nitrogen compound or phenol or ketone	4,214	67.9	100	NR	100	NR
Phenol	1,992	32.1	30	NR	20	NR
LC6b Ketone	2,074	22.6	NR	†(½)	½	111
Phenol	1,026	11.2	100	NR	NR	NR
Ether or acid	2,066	22.5	NR	†(½)	10	NR
Ketone or acid	1,992	21.7	NR	*	100	†(½)
Acid	2,037	22.2	NR	*	10	NR
Total correct out of 13			8	8	11½	6½

NR = Not reported.

* Category identified but intensity not given. Category assignment made by RTI on the basis of contractors' data.

In each of these cases half credit was given:

† ("C") category of ketone was identified but was based on 9-fluorene-4-carboxylic acid and not 9-fluorenone.

("D") Category of ketone identified by assignment was based on 9-fluorenone and not 9-fluorenone-4-carboxylic acid; ("B") acid category of ether or acid identified, but assignment was based on 9-fluorenone-4-carboxylic acid and not *o*-phenoxybenzoic acid. Also ketone category was identified but assignment was based on 9-fluorenone-4-carboxylic acid and not 9-fluorenone.

NOTE: Categories missed by all contractors: none.

Table 7. Categories Correctly Identified by Contractors in LC5 and LC6 Test Samples by LRMS

Category	mg/L	Weight %	Contractor			
			A	B	C	D
LC5 Fused alternate, nonalternate hydrocarbons	1,748	8.6	10	NR*	20	20
Heterocyclic nitrogen compounds	17,042	83.9	110	160	430	120
Ketone	1,522	7.5	111	100	20	111
LC6 Ketone†	7,027	41.1	200	100	30	10
Acid†	8,975	52.5	NR	40	110	NR
Phenol	1,078	6.3	NR	NR	10	10
Total correct out of 6			4	4	6	5

NR = Not reported.

* Although a compound belonging to this category was identified, the category itself was not listed.

† 9-Fluorenone-4-carboxylic acid was placed in acid category.

To distinguish differences in contractors' interpretations of the test spectra and samples and to identify sources of interpretation errors, two specific elements of the interpretation were examined. The contractors' LRMS signal assignments for the molecular ions in the spectra were compared (Tables 10 and 11) and all of the ions (molecular and fragment) assigned by the contractors to the compounds they correctly identified were compared (Tables 12 and 13). Five types of LRMS interpretation errors were observed:

1. Errors of omission—not noting the presence of molecular ions.
2. Reporting molecular ions as fragment ions.
3. Reporting fragment ions as molecular ions.
4. Incorrectly identifying molecular ions.
5. Incorrectly assigning ions to a homologous series.

Failure to find molecular ions accounted for almost half the categories and compounds missed in the test spectra and mixtures (Table 14).

In general, the contractors' category assignments for compounds identified in the tar sample were consistent with those expected to elute in these fractions as well as in fair agreement with results from a limited analysis of the sample by capillary column gas chromatography and mass spectrometry (Tables 15 and 16). Significant carryover of fused alternate hydrocarbons from earlier fractions was observed by Contractor A. Some disparity in the extent of spectral interpretation is evident if the molecular weight ranges reported by the contractors are examined (Table 17). The somewhat higher mass ranges reported by Contractor A were due primarily to the influence of higher molecular weight compounds carried over from fractions 2 and 3. Contractor C's narrow range of masses reported for fraction 6 was found to be due to the analyst failing to report data for the probe inlet spectrum of this fraction. The compounds reported were those detected by batch inlet. Although Contractor B did not interpret the tar sample spectra very thoroughly, many of the compounds reported by the other contractors were present in this contractor's spectra.

Table 8. Compounds in the IR/LRMS Spectral Interpretation Test Correctly Identified by LRMS

Compound	MW	mg/L	Weight %	Contractor			
				A	B	C	D
LC4a Naphthalene	128	980	6.2	10	NR	10	10
Anthracene	178	5,868	37.1	100	*	100	100
9-Methyl anthracene	192	3,980	25.1	100	*	100	100
Phenanthrene	178	980	6.2	100	*	100	100
9, 10-Dimethyl anthracene	206	4,027	25.4	100	*	100	10
LC4b Naphthalene	128	5,880	35.0	10	NR	10	100
Anthracene	178	3,920	23.3	100	*	100	100
9-Methyl anthracene	192	986	5.9	10	*	10	100
Phenanthrene	178	3,928	23.4	100	*	100	100
9, 10-Dimethyl anthracene	206	1,034	6.2	10	*	10	10
2, 3-Dimethyl naphthalene	156	1,065	6.3	10	NR	10	10
LC5a Fluorene	166	1,964	9.1	NR	NR	NR	NR
2,3-Benzofluorene	216	1,052	4.9	NR	NR	10	NR
n-Ethyl carbazole	195	11,265	52.1	NR	NR	100	100
2-Methyl indole	131	1,937	9.0	10	NR	10	10
Carbazole	167	4,328	20.0	100	NR	100	100
2,3-Dimethyl indole	145	1,054	4.9	10	NR	10	10
LC5b 7,8-Benzoquinoline	179	2,155	16.1	100	*†	100	100†
Phenanthradine	179	4,002	30.5	100	*†	100	100†
1,10-Phenanthroline	180	2,032	15.5	NR	NR	NR	NR
Phenazine	180	3,956	30.2	NR	NR	100	NR
Anthrone	194	1,016	7.7	NR	NR	NR	NR
LC6a 2-Hydroxy pyridine	95	4,214	67.9	100	NR	100	NR
2,6-Dimethyl phenol	122	1,022	16.5	10	NR	10	NR
6-6-Biphenol	186	970	15.6	10	NR	10	NR
LC6b 9-Fluorenone	180	2,074	22.6	NR	NR	NR	NR
2,6-Dimethyl phenol	122	1,026	11.2	NR	NR	NR	NR
o-Phenoxy benzoic acid	214	2,066	22.5	NR	NR	10	NR
1-Fluorene carboxylic acid	210	2,037	22.2	NR	*	10	NR
9-Fluorenone-4-carboxylic acid	224	1,992	21.7	NR	*	100	NR
Total correct out of 30				19	12	25	17

NR = Not reported.

*Compound was reported but intensity was not reported as required by Level 1.

†Credit was given for assignment of isomers of actual test spectra compounds. For example, assignment of ethyl anthracene was considered correct although dimethyl anthracene was the actual compound. Also, credit was given here for the assignment of acridine instead of 7,8-benzoquinoline and phenanthradine because all three are isomers and have nearly identical mass spectra.

NOTE: Compounds missed or incorrectly identified by all contractors: fluorene, 1,10-phenanthroline, anthrone, 9-fluorenone, and 2,6-dimethyl phenol.

In general, signal assignments for the tar sample (Table 18) were based on molecular ions only with supportive evidence given by the finding of other members of an alkylated homologous series. It is difficult to determine solely on the basis of the tabulated data which identifications are justified and which are not because many of the series overlap.

Factors other than errors in assignment and errors of omission, which, in general, affect analysis accuracy

include the approach to interpretation taken and the degree of interaction with the IR analyst to produce a composite report on the sample. The analyst's experience (years spent as a mass spectroscopist) and the time given to interpretation had little bearing on the results. A composite list of the major factors that correlate either positively or negatively with the more successful spectral interpretations include as positive correlates the search for molecular ions, the search for the eight

most abundant fragment ions, the setting of intensity and mass/charge range criteria for peaks to be studied in a spectrum, the use of the tabulated reference source, the *Eight Peak Index of Mass Spectra*, and the careful consideration of the IR data analyses in making final compound class/compound assignments (Table 19).

Excessive rigid dependence on the LC fraction number as a determining factor for accepting or rejecting compounds and compound classes was found to be a problem for several contractors. It is not possible for compounds from one category to elute over as many as four LC fractions. However, the majority of the compounds from this category should still be observed in the correct LC fraction. Also, individual compounds in general should elute within ± 1 fraction of the expected. Usually, if an individual compound is observed in more than three LC fractions, i.e., the expected and those on either side, then either the compound identification is wrong or the LC separation is unsatisfactory. The only case where such an elution would be expected is if the great majority of the sample loaded onto the column is one compound (e.g., 50 mg of anthracene). Needless to say, this seldom occurs in real assessment samples. Therefore, although the LC separation data are generally very useful for delineating the presence of individual compounds, they should still be used with caution to evaluate the presence or absence of compound classes.

After reviewing the IR interpretation results, the LRMS analysts in many cases revised their observations by adding new categories and/or compounds and by confirming or rejecting the presence of those already listed based on the LRMS alone (Table 20). In nearly every case these changes enhanced the quality of the data.

LRMS Recommendations

Five recommendations regarding LRMS measurement and spectral interpretation have been developed. These are:

1. Low (15 eV) ionizing voltage can be used to aid in the identification of molecular ions although this is not essential. It is especially useful if the 70 eV spectrum does not permit relatively straightforward interpretation.

Table 9. Compounds Correctly Identified by Contractors in LC5 and LC6 Test Samples by LRMS

	Compound	MW	mg/L	Weight %	Contractor			
					A	B	C	D
LC5	Fluorene	166	908	4.5	NR	NR	10	10
	2,3-Benzofluorene	216	840	4.1	NR	NR	10	10
	7,8-Benzoquinoline	179	3,936	19.4	100*	100*	100	100*
	1,10-Phenanthroline	180	6,294	31.0	NR	NR	10	NR
	Phenazine	180	3,405	16.8	NR	NR	100	NR
	2,6-Dimethyl quinoline	157	3,407	16.8	NR	30	100	10
	Anthrone	194	1,522	7.5	10	NR	NR	NR
LC6	9-Fluorenone	180	4,461	26.1	100	100	10	10
	1-Fluorene carboxylic acid	210	1,888	11.1	NR	NR	10	NR
	9-Fluorenone-4-carboxylic acid	224	7,087	41.5	NR	40	100	NR
	2-Methyl-1-tetralone	160	892	5.2	NR	NR	10	NR
	2-t-Butyl phenol	150	1,078	6.3	NR	NR	10	10
	2-Methyl-1,4-naphthoquinone	172	1,674	9.8	NR	NR	10	NR
Total correct out of 13								
					3	4	12	6

NR = Not reported.

*Phenanthradine and acridine are isomers of 7,8-benzoquinoline and were considered correct identifications here.

- Analysts who do not have the instrumental capability to switch from 70 eV to 15 eV during a run should be allowed to use chemical ionization (CI) mass spectrometry if and only if it can be established that CI provides significantly more information on molecular ions than 70 eV EI spectra.
- The *Eight Peak Index of Mass Spectra* should be used to interpret and verify spectra. Other reference sources such as the *EPA/NIH Data Base* (Heller and Milne, U.S. Department of Commerce, 1978), *The Mass Spectral Correlation Tables*, and the *American Petroleum Institute Index* are useful for certain cases but, as general references, they tend to be less complete or inaccurate.
- Peak intensity and m/e range criteria should be set above which all ions will be as fully accounted for as possible. These criteria may vary from sample to sample and from spectrum to spectrum.
- A series of spectra should be obtained as a sample is being volatilized from the probe. The spectra should be examined individually as well as in relation to each other.

In addition, several recommendations have been developed that apply to both IR and LRMS techniques:

- The LC fraction table in the Level 1 Manual or any other such similarly constructed table should not be used to exclude the presence of any category. Such a table should only be used as a very rough guide to verify the presence of a category or compound already indicated on the basis of more reliable factors such as IR and LRMS data.
- The IR and LRMS analysts should first analyze their data independently and then consult with one another to produce a composite report. Irreconcilable differences should be noted and both categories identified should be reported if the differences cannot be resolved.
- Analysts should adhere rigidly to the nomenclature for categories given in the Level 1 Manual. Nomenclature for compound identification must be uniform and not based on personal preferences. The International Union of Pure and Applied Chemists nomenclature for compounds should be used by all contractors.

- All LRMS and IR data should be reported on the Level 1 forms exactly as specified.
- Contractors should familiarize themselves with the sample source they are studying and the chemistry, if any, taking place. Under no circumstances should the analysts limit themselves to a "list of compounds" they believe will probably be present.
- In general, the LRMS and IR data should be used as primary data inputs to sample interpretation. Other inputs, such as LC fraction, sample source, and previously generated data on similar sources, should be given less weight.
- Polyfunctional compounds like 9-fluorenone-4-carboxylic acid should be listed as both possible categories (in this case, acid and ketone). Quantitation in such cases should be investigated.
- All contractors performing Level 1 LRMS and IR analyses should be given the opportunity to complete spectral interpretation tests on appropriate real and synthetic test samples that will measure the contractor's analytical and interpretive abilities. To relate the test results to actual sample analyses, these tests must have cost/time considerations. Some idea must be given of the intensity of the application of the technique.
- In conjunction with 8, all contractors performing Level 1 LRMS and IR analyses should receive guidelines documents illustrating efficient and accurate ways in which Level 1 LRMS and IR can be performed. These guidelines should contain numerous completely worked out example spectra. Also, along with these training sets, workshops should be held during which Level 1 LRMS and IR experts will interact and exchange ideas.

The implementation of 1 through 9 will improve the quality of the data generated by contractors now performing Level 1 LRMS and IR as well as aid those laboratories just beginning Level 1 work.

Table 10. Contractors' LRMS Signal Assignments for Specific Molecular Ions in the LRMS Test Spectra

Fraction	Ion	Expected	Contractor			
			A	B	C	D
LC4a	128	Naphthalene	Naphthalene	NA	Naphthalene	Naphthalene
	178	Anthracene, phenanthrene	Anthracene, phenanthrene	Anthracene, phenanthrene	Anthracene or phenanthrene	Anthracene or isomer
	192	9-Methyl anthracene	Methyl anthracene or methyl phenanthrene	Methyl anthracene	Methyl anthracene or methyl phenanthrene	Methyl anthracene or isomer
	206	9,10-Dimethyl anthracene	Dimethyl anthracene or phenanthrene	Dimethyl- or ethyl anthracene or phenanthrene	Dimethyl anthracene or dimethyl phenanthrene	Ethyl anthracene or isomer
LC4b	128	Naphthalene	Naphthalene	NA	Naphthalene	Naphthalene
	178	Anthracene, phenanthrene	Anthracene, phenanthrene	Anthracene, phenanthrene	Anthracene or phenanthrene	Anthracene or isomer
	192	9-Methyl anthracene	Methyl anthracene or phenanthrene	Methyl anthracene	Methyl anthracene or phenanthrene	Methyl anthracene or isomer
	206	9,10-Dimethyl anthracene	Dimethyl anthracene or phenanthrene	Dimethyl- or ethyl anthracene or phenanthrene	Ethyl anthracene or ethyl phenanthrene or dimethyl anthracene or dimethyl phenanthrene	Ethyl anthracene or isomer
	156	2,3-Dimethyl naphthalene	Dimethyl naphthalene	NA	Dimethyl naphthalene	Dimethyl naphthalene
LC5a	166	Fluorene	Fragment of phenanthridone, carbazole, methyl carbazole	NA	Fragment of carbazole, ethyl carbazole, or dimethyl carbazole	NA
	216	2,3-Benzofluorene	Unidentified	NA	Methyl pyrene or benzo-fluorene	NA
	195	n-Ethyl carbazole	Phenanthridone, acridone	Acridone	Ethyl carbazole or dimethyl carbazole	Ethyl carbazole
	131	2-Methyl indole	Methyl indole	NA	Methyl indole	Methyl indole
	167	Carbazole	Carbazole	Acridone fragment ion	Carbazole	Carbazole
LC5b	145	2,3-Dimethyl indole	Dimethyl indole	NA	Dimethyl indole	Ethyl indole
	179	7,8-Benzoquinoline, phenanthradine	Benzoquinoline, phenanthradine	Acridine	7,8-Benzoquinoline or phenanthridine	Acridine
	180	1,10-Phenanthroline; phenazine	Fluorenone	Fluorenone	Phenazine, fragment of anthraquinone or dimethyl benzo[c]cinnoline	Fluorenone
	194	Anthrone	Methyl fluorenone	Methyl fluorenone	Methyl benzoquinoline or methyl benzo[c]-cinnoline	Methyl fluorenone
LC6a	95	2-Hydroxy pyridine	Hydroxy pyridine	NA	2-Pyridone	Phenyl ether fragment
	122	2,6-Dimethyl phenol	Cresol, ethyl phenol	NA	Dimethyl phenol	Phenyl ether fragment
	186	6-6-Biphenol	Biphenyldiol (6-6-biphenol)	NA	6-6-Biphenol	Phenyl ether
LC6b	180	9-Fluorenone	NA	NA	NA	NA
	122	2,6-Dimethyl phenol	NA	NA	o-Phenoxy benzoic acid fragment	NA
	214	o-Phenoxy benzoic acid	NA	NA	o-phenoxy benzoic acid	NA
	210	1-Fluorene carboxylic acid	NA	Carboxy fluorene	Fluorene carboxylic acid	Methyl xanthone
	224	9-Fluorenone-4-carboxylic acid	Hydroxyanthraquinone	Carboxy fluorenone or carboxy methyl fluorene	9-Fluorenone-4-carboxylic acid	Dimethyl or ethyl xanthone

NA = Not assigned.

Table 11. Contractors' LRMS Signal Assignments for Specific Molecular Ions in the Low Resolution Mass Spectra They Generated from the Test Mixtures

Fraction	Ion	Expected	Contractor			
			A	B	C	D
LC5	166	Fluorene	NA	NA	Fluorene, fragment of methyl phenanthroline or methyl benzo[c]cinoline	Fluorene
	216	2,3-Benzofluorene	Methyl pyrene	NA	2,3-Benzofluorene or methyl pyrene	Benzofluorene
	179	7,8-Benzoquinoline	Acridine, phenanthridine, etc.	Acridine	Benzo[h]quinoline, acridine; phenazine and 1,10-phenanthroline fragment	Acridine
	180	1,1-Phenanthroline, phenazine	Fluorenone	Fluorenone or methyl-fluorene	Phenazine, 1,10-phenanthroline, anthraquinone fragment	Fluorenone
	157	2,6-Dimethyl quinoline	NA	Dimethyl quinoline	Dimethyl quinoline	Dimethyl or ethyl quinoline
	194	Anthrone	Anthrone	NA	Methyl phenanthroline or methyl benzo[c]cinnoline; fragment of methyl benzoquinoline or beta-naphthaquinoline	Methyl fluorenone
LC6	180	9-Fluorenone	Fluorenone	Fluorenone	Fluorenone or 1-phenalenone	Fluorenone
	210	1-Fluorene carboxylic acid	Unknown	NA	Fluorene carboxylic acid	NA
	224	9-Fluorenone-4-carboxylic acid	Hydroxy anthraquinone	Carboxy fluorenone	9-Fluorenone-4-carboxylic acid	NA
	160	2-Methyl-1-tetralone	NA	NA	Methyl tetralone	NA
	150	2-t-Butyl phenol	Fluorenone fragment	NA	t-Butyl phenol; fragment of fluorenone or 1-phenalenone; fragment of 9-fluorenone-4-carboxylic acid	t-Butyl phenol
	172	2-Methyl-1,4-naphthoquinone	Ethoxy naphthalene	NA	Methyl naphthoquinone	NA

NA = Not assigned.

Table 12. LRMS Signal Assignments for Compounds in the Spectral Interpretation Test Spectra

Compound	MW	Weight %	Contractor			
			A	B	C	D
LC4a Naphthalene	128	6.2	128	NR	128,127,129,64,51,126,102,63	128
Anthracene	178	37.1	178,179,176,89,152,151,150,177	178	178,176,179,89,76,88,151,152	178
9-Methyl anthracene	192	25.1	192,191,189,193,94.5	192,206,191	192,191,189,193,94.5,96,82.5,190	192
Phenanthrene	178	6.2	178,179,176,89,152,151,150,177	178	178,176,179,89,76,88,151,152	178
9,10-Dimethyl anthracene	206	25.4	206,191,205,207,189,165,202,203,204	192,206,191	206,191,207,189,89,192,101,82.5	206

Table 12. (cont'd)

	Compound	MW	Weight %	Contractor			
				A	B	C	D
LC4b	Naphthalene	128	35.0	128	NR	128,127,129,64, 51,126,102,63	128
	Anthracene	178	23.3	178,179,176,89, 152,151,150	178	178,179,176,89, 177,152,151,76	178
	9-Methyl anthracene	192	5.9	192,191,189,193, 94.5	192,206	192,191,189,193, 94.5,96,82.5,190	192
	Phenanthrene	178	23.4	178,179,176,89, 152,151,150,177	178	178,179,176,89, 177,152,151,76	178
	9,10-Dimethyl anthracene	206	6.2	206,191,205,189, 202,203,204,207, 165	192,206	206,191,207,189, 89,192,101,82.5	206
	2,3-Dimethyl naphthalene	156	6.3	156,141	NR	156,141,155,115, 157,142,76,153	156
LC5a	Fluorene	166	9.1	NR	NR	NR	NR
	2,3-Benzofluorene	216	4.9	NR	NR	216,215,94.5,217, 108,213,202,107.5	NR
	n-Ethyl carbazole	195	52.1	NR	NR	180,195,152,166, 140,139,151,196	195
	2-Methylindole	131	9.0	130,131	NR	130,131,65,77,51, 103,78,102	131
	Carbazole	167	20.0	167,166,139	NR	167,166,168,83.5, 139,63,69.5	167
	2,3-Dimethylindole	145	4.9	144,145	NR	144,145,130,143, 77,115,146,103	145
LC5b	7,8-Benzoquinoline	179	16.1	179,150,151,152, 153	NR	179,178,180,89.5, 151,76,89,152	NR
	Phenanthradine	179	30.5	179,150,151,152, 153	NR	179,178,180,89.5, 151,76,89,152	NR
	1,10-Phenanthroline	180	15.5	NR	NR	NR	NR
	Phenazine	180	30.2	NR	NR	180,179,90,76, 153,128,63,154	NR
	Anthrone	194	7.7	NR	NR	NR	NR
LC6a	2-Hydroxy pyridine	95	67.9	95,67,41,51	NR	95,67,41,66	NR
	2,6-Dimethyl phenol	122	16.5	122,107,77,51	NR	122,107,121,77, 51,79,91	NR
	6-6-Biphenol	186	15.6	186,157,158,131, 139,128,129,127	NR	186,157,158,131, 187,139,128,185	NR
	9-Fluorenone	180	22.6	NR	NR	NR	NR
	2,6-Dimethyl phenol	122	11.2	NR	NR	NR	NR
	O-Phenoxybenzoic acid	214	22.5	NR	NR	121,214,51,77, 65,120,122	NR
	1-Fluorene carboxylic acid	210	22.2	NR	210,165	165,210,166	NR
	9-Fluorenone-4-carboxylic acid	224	21.7	NR	224,179	224,225,207,151, 179,152,139	NR

***D** listed fragment ions for all compounds reported. Thus, the corresponding fragments could not be differentiated.

Table 13. LRMS Signal Assignments for Compounds in the Spectral Interpretation Test Mixtures

	Compound	MW	Weight %	Contractor			
				A	B	C	D
LC5	Fluorene	166	4.5	NR	NR	166,165,82.5,167, 163,83,164,82	166
	2,3-Benzofluorene	216	4.1	NR	NR	216,215,217,94.5, 108,107.5,213,106.5	216
	7,8-Benzoquinoline	179	19.4	179,151,89	NR	179,178,89.5,151, 76,89,152	179
	1,10-Phenanthroline	180	31.0	NR	NR	180,179,154,153, 128,90,76,63	NR
	Phenazine	180	16.8	NR	NR	180,179,154,153, 128,90,76,63	NR
	2,6-Dimethyl quinoline	157	16.8	NR	157	157,115,142,39, 51,63	157
	Anthrone	194	7.5	193,194	NR	NR	NR
LC6	9-Fluorenone	180	26.1	180,152,151,150, 76,75	180	180,152,151,150, 126,76,63,51,50	180
	1-Fluorene carboxylic acid	210	11.1	NR	NR	210,166,165	NR
	9-Fluorenone-4-carboxylic acid	224	41.5	NR	224	224,207,196,179, 168,151,150,139	NR
	2-Methyl-1-tetralone	160	5.2	NR	NR	160,145,131,118, 90,39	NR
	2-t-Butyl phenol	150	6.3	NR	NR	150,135,107,91, 77,39	150
	2-Methyl-1,4-naphthoquinone	172	9.8	NR	NR	172,144,116,115, 104	NR

NR = Not reported.

Table 14. Errors Made by Contractors in Interpreting Low Resolution Mass Spectra They Generated from Test Samples LC5 and LC6

	Test mixture	Contractor				Total
		A	B	C	D	
1. Did not find molecular ion at all.	LC5	2	3	0	0	3
	LC6	2	4	0	4	9
2. Found molecular ion but left unidentified.	LC5	0	0	0	0	0
	LC6	1	0	0	0	1
3. Found molecular ion but identified compound incorrectly (either as fragment or as another compound).	LC5	3	2	1	3	8
	LC6	2	0	0	0	2
		10	9	1	7	23

Table 15. Categories Reported by Contractors in Coal Gasification for Sample

Category	Sum of compound intensities			
	Contractor			
	A	B	C	D
LC4				
Heterocyclic nitrogen compounds	230	NR	160	300
Fused alternate, nonalternate hydrocarbons	70	NR	NR	NR
Unclassified	60	NR	NR	NR
Aliphatic hydrocarbons	NR	*	NR	NR
Phenols	NR	NR	NR	200
LC5				
Aromatic nitrile	NR	NR	100	NR
Heterocyclic sulfur	NR	NR	30	NR
Phenols	110	NR	210	220
Ketones	200	NR	NR	40
Aliphatic hydrocarbons	NR	*	NR	NR
Unclassified	10	NR	NR	20
LC6				
Phenols	340	100	310	NR
Heterocyclic nitrogen compounds	60	NR	NR	510
Ketones	10	NR	NR	NR
Unclassified	10	NR	NR	10

NR = Not reported.

*Compound was reported but intensity was not reported as required by Level 1.

Table 16. Compounds Found in Tar Sample by GC/MS and Reported by Contractors

Category	Compounds	Contractor			
		A	B	C	D
Fused alternate, nonalternate hydrocarbons	Naphthalene	—	—	—	—
	2-Methyl naphthalene	—	—	—	—
	1-Methyl naphthalene	—	—	—	—
	C ₂ -naphthalenes	—	—	—	—
	Biphenyl	—	—	—	—
	Acenaphthylene	—	—	—	—
	Acenaphthene	—	—	—	—
	Fluorene	—	—	—	—
	Phenanthrene	—	—	—	—
	Anthracene	—	—	—	—
	Fluoranthene	10	—	—	—
	Pyrene	10	—	—	—
	Benzo(a)fluorene	—	—	—	—
	Benzo(b)fluorene	—	—	—	—
	Benzo(a)anthracene	10	—	—	—
	Chrysene + triphenylene	10	—	—	—
	Benzo(b)fluoranthene	—	—	—	—
	Benzo(e)pyrene	10	—	—	—
	Benzo(a)pyrene	10	—	—	—
	Perylene	10	—	—	—
Dibenzof(a,h)anthracene	—	—	—	—	
Indeno(1,2,3-Cd)pyrene	—	—	—	—	
Benzo(g,h,i)perylene	10	—	—	—	
Heterocyclic sulfur compounds	Benzo(b)thiophene	—	—	10	—
Heterocyclic oxygen compounds	Dibenzofuran	100	—	—	—
Heterocyclic nitrogen compounds	Carbazole	100	—	100	100
	Benzidine	—	—	—	—
	Alkyl pyridines	—	—	—	100
	Quinoline	10	—	—	100
	Alkylquinolines	10	—	—	100
	Alkyl benzoquinolines	—	—	—	—
	Acridine	10	—	—	100
Phenols	Phenol	100	—	100	100
	Cresols	100	—	100	—
	Xylenols	100	100	100	—
	<i>o</i> -Isopropylphenols	—	—	10	—
	Trimethyl phenol	—	—	10	—
Number agreeing with GC data excluding fused alternate, nonalternate hydrocarbons		8	1	7	6

Table 17. Molecular Weight Ranges Reported by Contractors for Coal Gasification Tar Sample

	Contractor			
	A	B	C	D
LC4	167-500	43-91	167-231	167-195
LC5	100-252	43-91	128-212	108-252
LC6	94-300	122	94-136	79-217

Table 18. LRMS Signal Assignments for Selected Compounds Reported by Contractors in the Coal Gasification Tar Sample

Compound	MW	Contractor			
		A	B	C	D
LC4					
Carbazole	167	167	NA, P	167, 166, 139, 83.5, 69.5	167, P
Dibenzocarbazole	267	267	NA, P	63, 39, 267	NA, NP
Naphthol	144	144	NA, P	NA	144
LC5					
Methyl naphthol	158	158	NA, NP	158, 157, 115, 129, 128, 127	158
LC6					
Phenol	94	94	NA, P	94, 39, 66, 65	NA, P
Cresol	108	108	NA, P	108, 107, 77, 79, 51, 39	NA, P
Ethyl/dimethyl phenol	122	122	122, 107, 94, 77	122, 107, 121, 39, 77, 51, 79	NA, P
Acridine	179	179	NA, P	NA, P	179
Quinoline	129	129	NA, P	NA, P	129
Pyridine	79	NA, P	NA, P	NA, P	79

NA = Not assigned.

NP = Not present in spectra.

P = Present in spectra.

Table 19. Low Resolution Mass Spectral Interpretation Data Inputs and How They are Used by Contractors

	Contractor			
	A	B	C	D
1. Looks for molecular ions	✓	✓	✓	✓
2. Looks for some fragment ions	✓	✓	✓	✓
3. Looks for eight most abundant ions	✓	✓	✓	✓
4. Accounts for all peaks above given intensity and m/e value	✓	✓	✓	most peaks
5. Finding homologous series very important	✓	✓	no	✓
6. Peak intensity ratios	✓	✓	no	✓
7. IR data given equal weight	no	no	no	no
8. LC data used to verify & exclude	✓	✓	no	✓
9. LC data used to verify only	no	no	✓	no
10. Eight peak Index used often	✓	no	✓	✓

✓ = agrees with input shown.

No = does not agree with input shown.

*NOTE: While this list of inputs is in agreement with the approaches described by the contractors in their communications with the study coordinator, the application of these inputs to the study spectra and samples deviated from the above, especially for Contractors B and D.

Table 20. Changes Made in LRMS Interpretations by the LRMS Analyst After Seeing IR Interpretations

Sample	A	B	C	D
(1) Test spectra				
LC4a	NC	NC	Anthracene major component Phenanthrene minor component Dimethylantracene major component	NC
LC4b	NC	NC	Anthracene, phenanthrene same amounts	NC
LC5a	NC	Acridone and fluorenone were changed to carbazole and ethyl carbazole	Carbazole confirmed Ethyl carbazole confirmed	NC
LC5b	NC	NC	Benzoquinoline favored over phenanthradine Phenazine major component Anthraquinone	Acridine, fluorenone added
LC6a	NC	Pyridone or pyridinol, pyrrole were listed; previously nothing	Pyridone confirmed	Antraquinone, 2-Hydroxy-anthraquinone added
LC6b	NC	NC	9-Fluorenone-4-carboxylic acid major component	NC
(2) Test mixtures				
LC5	(1) Changed fluorenone to benzocinnoline (2) Deleted anthrone due to poor IR match	NC	1,10-Phenanthroline minor Phenazine major Acridine minor 7,8-Benzoquinoline minor Anthraquinone minor 2,6-Dimethylquinoline minor	IR added by reason not given
LC6	Changed hydroxyanthraquinone to 9-fluorenone-4-carboxylic acid Added fluorene carboxylic acid	Carboxyfluorenone changed to 9-fluorenone-4-carboxylic acid	9-Fluorenone, instead of just "fluorenone" 9-Fluorenone-4-COOH major	Added aromatic acids
(3) Tar sample				
Tar LC4	NC	Carbazole listed instead of aliphatic hydrocarbons, carbonyl, nitrile	NC (IR suggested alcohols)	Ketones, fused ring hydrocarbons added
Tar LC5	NC	Carbonyl, sulfonate fused ring aromatic or hetero-aromatic added	NC (IR very weak)	Esters added
Tar LC6	NC	Aromatic amines, aliphatic	Phenol major component	Esters, acids, ketones

NC = No change from previous analysis.

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L. D. Johnson is the EPA Project Officer (see below).

The complete report, entitled "Collection and Interpretation of Level 1 IR and LRMS Data," (Order No. PB 80-217987; Cost: \$21.50, subject to change) will be available from:

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5285 Port Royal Road
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