



Project Summary

Standardization of EPA Method 8610, Part 2

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U.S. EPA Method 8610, "Total Aromatics by Ultraviolet Absorption" was evaluated in conjunction with U.S. EPA Method 3560, "Reverse Phase Cartridge Extraction" for the separation and semi-quantitative determination of visible or ultraviolet absorbing organic compounds listed in Appendix VIII of the Resource Conservation and Recovery Act (RCRA). In Part 1 of this program, reported separately, the following work was conducted:

- A data base of visible and ultraviolet (UV) spectral data for the Appendix VIII compounds was developed and used to estimate detection limits for those compounds which absorb UV or visible light in the region 220 to 700 nm.
- The reverse phase cartridge extraction procedure of Method 3560 was evaluated and modified for the separation of polar and non-polar subsets of 21 Method 8610 analytes using methanol and hexane eluents. However, the extraction procedure was found to be unsuitable for group separation in its present form, and the results indicated that non-overlapping group separation was probably chemically unattainable.
- The spectrophotometric determinative technique of Method 8610 was evaluated and found to be very sensitive for a majority of the compounds in the range of 220 to 400 nm.

Based on these Part 1 results, a Part 2 study was conducted to further investigate the applicability of these methods in a variety of ground-water samples and to refine method detection limit estimates.

Seven ground-water samples were supplied for the Part 2 study by ASTM Committee D-34 members. These samples were evaluated for background UV absorbance, and duplicate sample extractions were used to simulate down-gradient versus up-gradient testing. An estimated positive response decision level was found to be 0.02 absorbance units. Five Method 8610 analytes were evaluated for spike recoveries from both reagent water and a composite ground-water sample. One analyte was found to be unstable in water and the elution solvents used. The remaining four analytes had good total recoveries from reagent water ranging from 79 to 108 percent with standard deviations of all but one analyte ranging from 1 to 5 percent. Spike recoveries for composited ground water were not reproducible due, apparently, to a significant variability in recovery of native UV absorbing material. The cause of the variability could not be specifically attributed to, but may have been associated with, the presence of very finely divided (<20 micron particulate material).

This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The U.S. Environmental Protection Agency (EPA) has proposed an amendment (October 1, 1984, Federal Register) to its hazardous waste regulations under the Resource Conservation and Recovery Act (RCRA) consisting of a hierarchical

analysis procedure for ground-water testing. The proposed hierarchical procedure will allow hazardous waste facility operators to screen ground-water samples quickly for specific compounds using inexpensive methods, thus reducing their overall testing burden for regulated pollutants without jeopardizing environmental protection.

One of the proposed methods included in the hierarchical analysis protocol is EPA Method 8610, "Total Aromatics by Ultraviolet Absorption." When used in conjunction with EPA Method 3560, "Reverse Phase Cartridge Extraction," Method 8610 will allow operators of hazardous waste facilities to monitor ground water beneath their facilities for many regulated compounds. This screening data allows the operator to also make decisions for advanced testing.

To evaluate the usefulness of Methods 3560 and 8610, Battelle's Columbus Division, under Contract Number 68-03-1760, conducted a research program to: (1) generate a data base of ultraviolet and visible spectral data for Method 8610 analytes; (2) evaluate Method 3560 for the collection and separation of polar and nonpolar Method 8610 analytes; and (3) evaluate Method 8610 for the analysis of total aromatic compounds. The results of this work have been reported separately (c.f., Project Summary EPA/600/S4-85/052, December 1985). The results reported in this Project Summary are for a Part 2 continuation of the research program. Part 2 efforts involved: (1) acquisition of authentic ground-water samples from ASTM Committee D-34 members; (2) evaluation of matrix effects on ultraviolet determinative techniques using Method 8610; and (3) evaluation of recoveries and detection limits of selected Method 8610 analytes spiked into reagent water and ground-water samples containing significant UV background. For the purpose of this Project Summary, the reader's familiarity with the earlier work is assumed.

Experimental Procedures

Reagent water and ground-water samples tested in this work were extracted with a Baker-10 SPE vacuum manifold system and 6-ml disposal octadecyl (C18) solid-phase extraction (SPE) cartridges. Each SPE cartridge contained about 500 mg of sorbent specified to have a mean diameter of 600- μ m and a mean pore size of 60 Å. Samples were eluted with both methanol and hexane in all experiments. The methanol and hexane were obtained from Burdick & Jackson

and were used as received. Reagent water was generated from an in-house Milli-RO/Milli-Q® system.

UV analysis of methanol and hexane SPE eluates was conducted with a Cary 17DX recording UV/VIS spectrophotometer. This system has a short-term noise level of 0.001 absorbance units (a.u.) and a non-correctable baseline non-linearity of about ± 0.002 a.u. between 220 and 400 nm. Analyses of 20 SPE-extracted reagent water method blanks indicated the system's overall spectral variability to be approximately 0.005 a.u. between 230 and 400 nm.

Results and Discussion

Evaluation of Ground-Water Matrix Effects

Seven ground-water samples were contributed by ASTM Committee D-36 members. Three samples contained no particulate matter and had the appearance of ordinary drinking water. Two samples contained a moderate amount of particulate matter, and the remaining two samples contained a significantly greater amount of particulate matter. In all samples, the particulate matter appeared to settle completely on overnight standing. The UV spectra of methanol and hexane SPE eluates of the seven ground-water samples were examined two ways: (1) versus a reagent water blank to determine the UV spectra of the SPE recovered material, and (2) versus a second replicate of the same ground water to simulate a down-gradient versus up-gradient monitoring situation. Up-gradient ground water is that moving towards a disposal site; down-gradient ground water is that moving away from a disposal site. For the methanol SPE eluates, three of the ground-water samples were found to have very low UV background (0.03 a.u.), three had slightly higher levels (0.04 to 0.06 a.u.), and one had a distinctly higher level (0.25 a.u.). All of the ground-water hexane SPE eluates were indistinguishable from those produced with reagent water. For the methanol eluates, the simulated down-gradient versus up-gradient UV spectra gave the following average absorbance differences for the seven ground waters: 0.012 ± 0.005 a.u. at 230 nm, 0.009 ± 0.005 a.u. at 250 nm, and 0.008 ± 0.004 a.u. at 280 nm. Thus, the absorbance difference required to conclude that a given down-gradient water sample contains higher levels of UV absorbing material than a corresponding up-gradient sample varies with the wavelength used. For wavelengths

between 230 and 300 nm, about 0.02 a.u. difference is indicated by these limited results. Similarly, between 300 and 400 nm, about 0.01 a.u. difference would be required.

Spike Recoveries From Reagent Water

Percent recoveries from reagent water for five Method 8610 analytes spiked at two levels are shown in Table 1. In these experiments, each analyte was spiked individually into 100 mL of water using 50 μ L of a methanolic spiking standard. After mixing, the 100-mL sample was extracted using the SPE cartridge, and UV analysis was conducted on the resulting methanol and hexane eluates. Calibration standards were prepared by spiking methanol and hexane eluates of reagent water blanks with the same spiking mixture as for samples (i.e., 100 percent recovery standards). The results shown in Table 1 support three conclusions:

- Overall recovery efficiency of the SPE extraction is adequate for essentially all purposes.
- Separate recovery of apolar analytes in the hexane eluate is clearly not feasible when the first elution solvent is as strongly eluting as methanol.
- There is apparently more variability due to uncontrolled aspects of the sequential elution than there is in the SPE cartridge extraction efficiency (i.e., precision of the methanol or hexane eluates versus that of the total by individual replicate).

Spike Recoveries From Composite Ground Water

To provide a sufficiently large homogeneous sample for testing ground-water spike recoveries, four of the individual ground-water samples were combined. The samples selected for compositing were the four with the highest SPE recoveries of background UV-adsorbing material so that a maximum challenge to Methods 3560 and 8610 would be obtained. Sample compositing produced a substantial change in the morphology of the particulate matter. Whereas, the particulate matter in the individual ground-water samples settled rapidly, particulate matter in the composite ground water would not fully settle even on overnight standing. Also, in contrast to the individual ground-water samples, a small but variable amount of the particulate matter was recovered in the

TABLE 1. Recoveries of Selected Analytes From Reagent Water

Compound	Amount Spiked, ^(a) μg/L	Percent Recovery											
		Methanol SPE ^(b) Eluate				Hexane SPE Eluate				Sum of SPE Eluates			
		Replicate			Mean ±SD ^(c)	Replicate			Mean ±SD	Replicate			Mean ±SD
Polar Aromatic Compounds													
3-3'-Dichlorobenzidine	23	88	85	85	86±1.7	0	0	0	—	88	85	85	86±1.7
	116	95	88	95	93±4	0	0	0	—	95	88	95	93±4
2,4-Dimethylphenol	150	94	94	100	96±4	3	3	0	2±2	97	97	100	98±1.7
	750	93	89	87	90±3	2	3	4	3±1	95	92	91	93±2.1
1,2-Diphenylhydrazine ^(d)	15	100	100	100	100±0	10	10	0	7±6	110	110	110	106±6
	75	98	87	98	94±6	5	10	9	8±3	103	97	107	102±5
Nonpolar Aromatic Compounds													
1,4-Dichlorobenzene	600	71	79	86	79±8	19	14	10	14±5	90	93	96	93±3
	3000	68	67	70	68±1.5	10	12	10	11±1	78	79	80	79±1
Methoxychlor	30	64	72	55	64±9	64	28	42	45±18	128	100	97	108±17
	150	53	55	51	53±2	13	39	33	28±14	66	94	84	81±14

^(a) The low and high spike levels were based on the λ_{max} absorbivity for each analyte so that the lower level was three to five times an estimated detection limit; the higher level was five times the lower level.

^(b) SPE: solid phase extraction.

^(c) SD: standard deviation.

^(d) This analyte is unstable under aqueous acidic conditions; the actual species measured is probably benzidine.

methanol SPE eluates from the composite ground-water sample. The UV spectra obtained from the methanol SPE eluates of the spiked and nonspiked composite ground water all supported the same conclusion: variable amounts of matrix UV-absorbing material were recovered in the methanol SPE eluates which superimposed an absorbance baseline to shift the observed absorbances to either higher or lower values than the correct ones. In some cases, baselines for nonspiked samples, shifted with a positive bias, were actually above a low-spike UV maximum shifted with a negative bias giving a negative net absorbance and, therefore, a negative recovery. An example of this effect is shown for dichlorobenzene in Figure 1, along with the corresponding result for reagent water.

Since the spectral variations of methanol SPE eluates of nonspiked composite ground-water samples all had similar wavelength/intensity profiles, a baseline correction was made based on a visually approximated baseline bias for each spectrum of spiked replicates to give a more accurate representation of the actual spike recoveries obtained. The results using these pseudo-baselines are shown in Table 2. While the methanol

eluate recoveries shown in Table 2 for the composite ground water compare favorably with those of Table 1 for reagent water, the use of pseudo-baselines prevents any detailed comparisons between these methanol eluate data sets. The hexane SPE eluates from the composite ground water did not produce a similar

nonreproducible baseline bias. However, the recovery values obtained do show some significant differences between reagent water and composite ground water for methoxychlor. Averages of 44 and 28 percent were recovered in the low and high spike samples, respectively, for reagent water, compared to 5 and 6

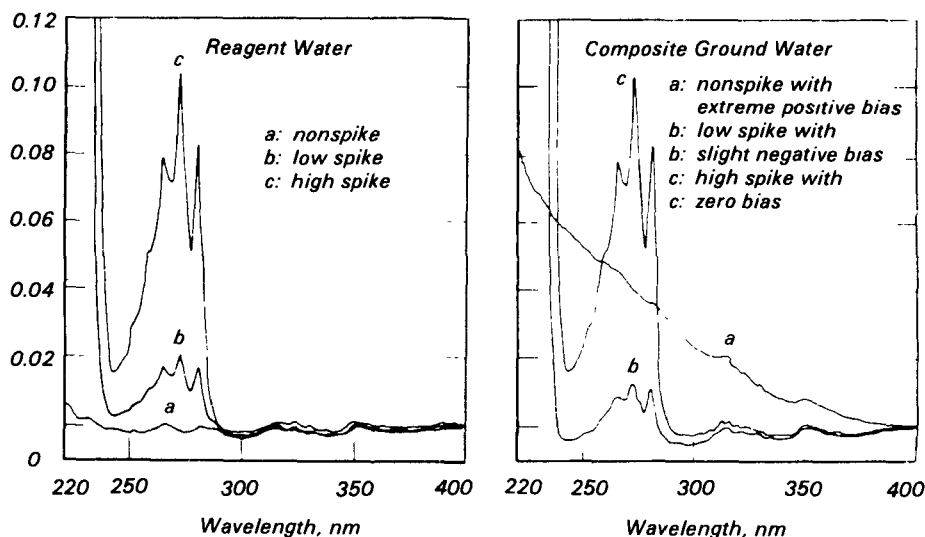


Figure 1. UV spectra of methanol eluates from reagent water and composite ground water.

TABLE 2. Recoveries of Selected Analytes From Composite Ground Water

Compound	Amount Spiked, ^(a) µg/L	Percent Recovery											
		Methanol SPE ^(b) Eluate				Hexane SPE Eluate				Sum of SPE Eluates			
		Replicate			Mean ±SD ^(c)	Replicate			Mean ±SD	Replicate			Mean ±SD
	1	2	3		1	2	3		1	2	3		
Polar Aromatic Compounds													
3,3'-Dichlorobenzidine	15	81	62 ^(e)	58	67±12	0	0	0	—	81	62	58	67±12
	75	87	74 ^(e)	85	82±7	0	0	0	—	87	74	85	82±7
2,4-Dimethylphenol	150	110 ^(e)	105 ^(e)	115 ^(e)	110±5	0	0	0	—	110	105	115	110±5
	750	115 ^(e)	91 ^(e)	121 ^(e)	109±16	0	2	0	1±1	115	93	121	110±15
1,2-Diphenylhydrazine ^(d)	15	NO	143 ^(e)	171 ^(e)	160	25	25	37	29±7	25	168	208	130±90
	75	74	74	74	74±0	19	21	19	20±1	93	95	93	94±1
Nonpolar Aromatic Compounds													
1,4-Dichlorobenzene	600	86 ^(e)	86 ^(e)	71 ^(e)	81±9	14	14	14	14±0	100	100	85	95±9
	3000	72 ^(e)	80 ^(e)	70 ^(e)	74±5	14	12	13	13±1	86	92	83	87±4
Methoxychlor	30	36 ^(e)	36 ^(e)	32 ^(e)	35±2	7	0	7	5±4	43	36	39	39±4
	150	52 ^(e)	47 ^(e)	47 ^(e)	49±3	6	7	4	6±2	58	54	51	54±4

^(a) See footnote (a), Table 1; the levels for 3,3'-dichlorobenzidine were adjusted downward for these experiments based on the reagent water results.

^(b) SPE: solid phase extraction.

^(c) SD: standard deviation.

^(d) This analyte is unstable under aqueous acidic conditions; the actual species measured is probably benzidine.

^(e) Value obtained after making an approximate correction for baseline bias (see text).

percent recovered in the low and high spike samples for composite ground water. In contrast, there was no hexane eluate recovery difference between reagent water and ground water for the other nonpolar analyte, 1,4-dichlorobenzene, which averaged between 11 and 14 percent for all four data sets.

While the actual chemical mechanism causing the wide variability in recovery of the native UV absorbing material from composite ground-water samples cannot be identified from the data presently available, the cause of the variability can definitely be attributed to the ground water itself rather than laboratory procedural variations. The reasons are:

- The same lot of reverse-phase cartridges, elution solvents and spiking media were used for all experiments.
- All extracts were produced by the same laboratory technician using the same apparatus and identical laboratory procedures in the same laboratory location.
- Sets of extracts were generated sequentially with no time delay between the reagent water set and the ground-water set.
- Reagent water control blanks produced along with the ground-water

samples were uniformly identical to those obtained with the reagent water set.

Finely divided particulate material in the composite ground water is the mostly likely cause of the variable UV baseline bias. Although the extraction cartridges are equipped with a 20-µm polyethylene frit at the top and bottom, the suspended particulate matter was not completely removed as some of the particulate matter color was visible on the column bed. For the composite ground water, the methanol elution removed some of this particulate matter from the cartridge while none was recovered in methanol eluates of the non-composited ground waters. The recovery of particulate matter into the methanol eluate occurred for every non-spiked and spiked composite ground-water sample and was estimated to vary in amount over a range of a factor of three with the total amount present averaging about 0.5 mg. Of the amount of suspended particulate matter in the 100-mL aqueous sample, less than one percent is estimated to have been recovered in the methanol eluates.

While quantitative conclusions are not possible from the composite ground-water data, the results do suggest that removing particulate matter before ex-

traction might provide recovery results approaching those obtained for reagent water. Further experimentation on the composite ground water used was not possible, since it was consumed in the spiking experiments. However, it was possible to further examine the composite ground-water methanol eluates for evidence of the possible mechanisms by which the inorganic particulate matter could have caused the matrix recovery variability. Centrifugation and filtration (0.5 micron) of the three nonspiked methanol eluates with the highest matrix background recoveries were tested to determine if suspended particulate matter could be the cause of the variability observed. Composited methanol eluates of reagent water method blanks were used as the UV reference sample. Each of these three high background composite water methanol eluates was examined against the composite reference three times: (1) after settling for about 1 hour, (2) after centrifugation at 2300 rpm for 10 minutes, and (3) after filtration (0.5 micron). Centrifugation and filtration, versus the gravity-settled trial, had no effect on the UV trace for any of the three nonspiked composite ground-water methanol eluates. Therefore, particulate matter in the UV measurement beam

was probably not the cause of the recovery variability. To determine if the variability was caused by dissolved carbonate anion, these same methanol eluates were acidified with HCl and then purged with nitrogen to remove CO₂. However, since all three samples became yellow and more UV-opaque, this experiment provided no information.

Evaluation of Method 8610 Sensitivity

Because of the matrix UV recovery variability observed for the composite ground water, only the reagent water results are useful for predicting Method Detection Limits in the 230 to 400 nm range. If one assumes that the cause of the ground-water matrix problem could be identified and the problem rectified to provide reproducibilities comparable to those found for reagent water, an absorbance difference (down-gradient versus up-gradient) of 0.02 a.u. can be taken as the decision limit threshold. This decision level for a positive response is four times higher than the proposed Method 8610 decision limit of 0.005 a.u. Using the 0.02 a.u. threshold value, theoretical detection limits for Method 8610 analytes can be calculated. Additional assumptions made for these calculations are: (1) the use of a 100-mL ground-water sample, (2) an SPE eluent volume of 5.0 mL of methanol or hexane, (3) 100 percent recovery in a single SPE eluent, and (4) analysis without further concentration. Of the Method 8610 analytes for which estimated detection limits are thus calculated, only 28 percent of the 129 analytes have 10 µg/L or lower detection limits and 68 percent are estimated to have 50 µg/L or lower detection limits.

Conclusions

The results of this work support several conclusions regarding the performance of EPA Methods 3560 and 8610:

- Method 8610, in its present form, was not suitable for analyzing the tested composite ground-water sample. The tested water contained fine sediment particles which partially moved through the extraction cartridge and possibly interfered with the UV analysis. However, it was impossible to determine how the particles caused the poor reproducibility or even that it was, indeed, caused by some phenomenon associated with the particles.

- For reagent water, the simulated down-gradient versus up-gradient results suggest that a positive response of 0.02 a.u. in the UV range 230 to 400 nm is sufficient to indicate down-gradient contamination. This result is four times higher than the proposed Method 8610 decision limit of 0.005 a.u.
- Using extinction coefficients reported in Part 1 of this program, 0.02 a.u. as the positive response decision level, a 20-fold Method 3560 concentration factor, and recovery of 100 percent of an analyte in either the methanol or hexane eluent, it is estimated that only 28 percent of the Method 8610 analytes have a detection limit equal to or less than 10 µg/L and 68 percent have a detection limit equal to or less than 50 µg/L.
- Method 3560 was successful in recovering 3,3'-dichlorobenzidine, 2,4-dimethylphenol, 1,4-dichlorobenzene, and methoxychlor from reagent water with recoveries ranging from 79 to 108 percent. The first two analytes were almost completely eluted with methanol and the last two analytes were partially eluted in both methanol and hexane. The data obtained from ground-water spiking appear to support the same conclusion, but the non-reproducibility of the background UV material does not allow quantitative demonstration of that conclusion.

Recommendations

It is unlikely that any amount of method development will enable Methods 3560 and 8610 to adequately address most of the analytes assigned to them by the SW-846 Hierarchical Analytical Protocol (HAP) scheme. These methods may, however, be adequate for a significant enough subset to justify further method development. If so, then the following recommendations are offered for further method development:

- The effect on accuracy and precision of including a step in Method 8610 for removing particulate, either by filtration or centrifugation, before UV determination should be investigated to determine whether or not Method 3560/8610 can actually be applied to heterogeneous samples.
- Since the results of the previous study showed that polarity class separation with methanol and hexane elution solvents was probably not feasible, effort should be directed to

identify a single elution solvent, such as ethanol, isopropanol or a mixed system, which will give high recovery for all analytes in a single elution.

- Further work to improve the present 20-fold concentration factor and thereby increase the method sensitivity will be required to obtain a usable method. For example, use of 1.0 mL UV cells, 1.5 mL of elution solvent, and a 150-mL sample would provide a 100-fold concentration factor.
- Other commercially available reverse phase sorbents should be evaluated to determine whether a particular type provides superior recovery and precision of the method analytes.
- If the cause of reproducibility problems for ground water identified in this work can be identified and eliminated, an automated Method 8610 approach using an HPLC auto-sampler, UV detectors, and automated chromatography data system quantification should be developed since improved signal-to-noise and, therefore, lower detection limits should be possible than those demonstrated in this work using a double beam spectrophotometer.

