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Precision and Accuracy of Concurrent Multicomponent Multiclass Analysis of Drinking Water Extracts by GC/MS

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For economic reasons (primarily), analytical protocols for environmental contaminants at trace levels are often designed to obtain a maximum of information per analysis and hence are optimized for the analysis of general classes of compounds rather than for individual compounds. This pragmatic approach, which provides greater efficiency in the use of physical resources, produces results that may vary in precision and accuracy for individual components in a multicomponent analysis. The quality of the results may be even further compromised when multiple classes of compounds exhibiting similar chemical features are assayed concurrently. This is particularly true for analyses based on GC/MS where the GC parameters, MS parameters and method of quantitation must be set to provide the "best" overall results rather than the "best" result for an individual component. We have reported (Williams et al. 1982) in the past on methods for the analysis for chlorinated aromatics (CA), organochlorines (OC), polycyclic aromatic hydrocarbons (PAH) and organophosphates (OP) in drinking water using XAD-2 resin for the concentration prior to analysis by GC/MS. The present multilaboratory comparison study was undertaken to determine the quality of results obtained in the concurrent GC/MS analysis of artificially loaded samples containing CA, OC, PAH and OP.

MATERIALS AND METHODS

Ten master solutions containing from 11 to 18 compounds at concentrations in the range of 2 to 15 ng/μL were prepared from authentic standards. The lower limit of the concentration range was chosen to be above the estimated quantitation limit (ACS, 1980) for the analytical procedure. The number, the concentration and the selection of the analytes in each sample were selected at random from a group of 55 compounds (Table 1) representative of CA, OC, PAH and OP in drinking water. In order to simulate the solvent matrix in authentic drinking water extracts, the solvent (15%, v/v acetone/hexane) used for sample preparation was obtained (Lebel et al. 1979) as follows: a suitable volume of drinking water was passed through two XAD-2 resin cartridges connected in series; the second cartridge was eluted with 15%, v/v acetone/hexane; the eluate was concentrated and used to prepare the master

Table 1. Compounds analyzed

PAH

naphthalene
2-methylnaphthalene
1-methylnaphthalene
biphenyl
2-ethylnaphthalene
1-ethylnaphthalene
bibenzyl
cis-stilbene
2,3,6-trimethylnaphthalene
2,3,5-trimethylnaphthalene
fluorene
3,3'-dimethylbiphenyl
4,4'-dimethylbiphenyl
trans-stilbene
9-fluorenone
phenanthrene
anthracene
2-methylanthracene
9-methylanthracene
anthraquinone
fluoranthene
pyrene

CA

1,4-dichlorobenzene
1,2-dichlorobenzene
1,3,5-trichlorobenzene
1,2,3-trichlorobenzene
2,4,5-trichlorotoluene
1,3,4,5-tetrachlorobenzene
1,2,3,4-tetrachlorobenzene
pentachlorobenzene
hexachlorobenzene
octachlorostyrene

OC

α-hexachlorocyclohexane
γ-hexachlorocyclohexane
γ-chlordane
α-chlordane
aldrin
heptachlor epoxide
oxychlordane
dieldrin
p,p'-DDE
p,p'-DDT
photomirex
mirex

OP

triethylphosphate
tributylphosphate
tris(2-chloroethyl)phosphate
tris(1,3-dichloroisopropyl)phosphate
triphenylphosphate
2-ethylhexyldiphenylphosphate
tributoxyethylphosphate
o-isopropylphenyldiphenylphosphate
tri-o-tolylphosphate
p-t-butylphenyldiphenylphosphate
tri-p-tolylphosphate

solutions. Analysis of the eluate prepared in this manner showed no detectable signal at a detection limit of 0.5 ng injected for the 55 compounds in the present study. Aliquots of the ten solutions along with aliquots of two standard solutions containing all 55 analytes at known concentrations (ca. 4 ng/μL and ca. 13 ng/μL) were submitted to six independent laboratories for quantitative GC/MS analysis. Each laboratory stored the samples at ≤4°C in the interim period prior to analysis and analyzed for the 55 target compounds by using procedures of their choice. The analytical parameters (Table 2) varied from laboratory to laboratory for column selection and method of quantitation.

Table 2. Analytical Parameters

Laboratory	GC Column	Quantitation Technique
A	DB-1 (30 m x 0.25 mm i.d)	Internal Standard
B	SE-54 (30 m x 0.25 mm i.d)	Internal Standard
C	DB-5 (30 m x 0.25 mm i.d)	External Standard
D	DB-5 (15 m x 0.25 mm i.d)	External Standard
E	SE-54 (30 m x 0.25 mm i.d)	Internal Standard
F	DB-5 (30 m x 0.25 mm i.d)	Internal Standard

RESULTS AND DISCUSSION

The 10 samples submitted for analysis had been fortified with a total of 143 analytes distributed among the four compound classes as follows: 28 CA, 27 OC, 53 PAH and 35 OP. The six laboratories respectively reported values for 100%, 100%, 100%, 100%, 96% and 69% of the analytes. The results of the six laboratories are summarized in Table 3 where each entry represents the percentage of results that fell within the accuracy ranges listed (± 10% to ± 60%) when the gravimetrically determined and analytically determined quantities were compared. If the "missed" analytes are excluded from the statistical treatment, laboratory E would have reported 84% of their results within ± 60% of the fortification levels which is comparable to the performance of laboratory D. However, further examination of the results revealed that laboratory E was the only laboratory that was unable to detect all of the analytes in the standard solution (ca. 4 ng/μL). Laboratory E was unable to detect 45% of the analytes in the standard solution when ca. 8 ng of the analyte was injected, indicating poor instrument sensitivity for this laboratory at the time of the analysis. In view of the pronounced systemic error caused by the limit of detection being above the levels of fortification for many of the analytes the results of laboratory E were completely excluded from subsequent statistical treatments, as recommended by Youden & Steiner (1975). Laboratory D exhibited a poor performance at the ± 10 accuracy level (8% of results) which improved somewhat at the ± 60% accuracy level (80% of results). However, the results of laboratory D could not be related specifically to a deficiency in the performance of the analytical instrument as was the case for laboratory E. Hence, the results of laboratory D, though comparable or inferior to laboratory E, were retained in the statistical analysis. The remaining four laboratories produced more accurate results which were comparable to one another.

The average performance of laboratories A, B, C, D, and F was better for CA, OC and PAH than for OP (Table 4). On average only 65% of the OP results were within ± 60% of the gravimetric amounts compared to 100%, 96% and 93% for the CA, OC and PAH, respective-

Table 3. Percent accurate results[a] as a function of accuracy for individual laboratories

Percent Accuracy (+/-)	Laboratory A	B	C	D	E	F
10	27	36	30	8	17	39
20	59	66	57	20	33	57
30	75	81	75	38	43	72
40	85	84	82	52	52	82
50	87	84	89	71	55	87
60	90	89	92	80	58	90

[a] - percentage of results falling within the accuracy range

ly, which suggests that the OP analysis is subject to analytical errors to which the other compound classes are not. When the OP results were excluded (Table 5) an average 88% of the results were within ± 40% of the gravimetric amounts. The estimation of accuracy based on the comparison of analytical and gravimetric amounts incorporates uncertainties attendant with preparation and handling of the samples and the standard solutions prior to the analyses, as well as the actual analytical procedure. In order to obtain an estimation of the precision and accuracy of the GC/MS analysis exclusively, the treatment of Youden and Steiner (1975) using pairs of samples containing selected compounds at identical gravimetric concentrations was applied for 18 compounds representing all four compound classes; this treatment allows the analyst to divide the overall uncertainty into systematic and random components which are related to the accuracy and the precision of the analytical technique, respectively. The overall (S_d), systematic (S_b) and random (S_r) standard deviations reported as percent of the average analytical concentrations are shown in Table 6 according to compound class.

Table 4. Percent accurate results by compound class (laboratories A,B,C,D,F.)

Percent Accuracy (+/-)	CA	OC	PAH	OP
10	41	24	34	13
20	77	48	52	24
30	93	75	73	32
40	96	88	84	44
50	99	93	90	54
60	100	96	93	65

Table 5. Percent accurate results as a function of accuracy for individual laboratories excluding the OP analyses

Percent Accuracy (+/-)	Laboratory A	B	C	D	F
10	34	41	33	9	47
20	75	75	63	23	69
30	92	94	82	46	85
40	97	96	93	60	94
50	97	96	95	79	97
60	98	98	98	87	97

The average overall standard deviation for the OP is higher (± 38%) than for the combined CA, OC and PAH (± 24%) and the difference is significant statistically (at the 95% confidence level) for the sample size of the present study. The difference in the overall standard deviations is largely associated with the systematic standard deviations for the OP (± 28%) and combined CA OC and PAH (± 16%), which indicates that the loss of accuracy for the OP is associated with the analytical technique, most likely the gas chromatograph.

Table 6. Percent standard deviations (S_r-random, S_b-systematic, S_d-overall)

Compound Class	Number of Pairs	S_r	S_b	S_d
CA	2	10	16	25
PAH	7	8	16	25
OC	3	8	15	23
OP	6	11	28	38

In summary, concurrent multicomponent multiclass analysis at the low ng level can be peformed effectively by GC/MS for CA, OC and PAH with a confidence that ca. 90% of the results are within ± 40% of the true values. The OP, on the other hand, can be determined with a lower accuracy (ca. 65% of the results within ± 60% of the true values).

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