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Project Summary

Fused Silica Capillary Column GC/MS Quality Control Protocol for the Determination of Semivolatile Priority Pollutants

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This quality control protocol is intended to serve as a reference document for those laboratories employing fused silica capillary column (FSCC) gas chromatographic/mass spectrometric (GC/MS) techniques for the analysis of the extractable semivolatile priority pollutants in all environmental matrices. The document presents apparatus requirements and gives guidance for standards preparation, as well as instrument setup and calibration. Reference information, including internal standard assignment, quantitation mass, relative retention times (RRT) values, interlaboratory and intralaboratory response factor (RF) values, is also presented. This document provides a schedule for GC/MS system calibration requirements including ion abundance calibration, column performance testing, sensitivity verification, system linearity, and injection technique reproducibility.

This protocol does *not* provide guidance regarding sample extraction and workup; therefore, any quality control (QC) parameters related to this aspect of the analysis are not addressed in this protocol.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is full documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Fused Silica Capillary Column (FSCC) Gas Chromatography/Mass Spectrometry (GC/MS) has been shown to provide an effective instrumental analysis configuration for the determination of semivolatile priority pollutants in extracts of environmental samples and hazardous wastes. FSCC GC/MS is employed by various EPA programs in classifying materials as hazardous/non-hazardous for organic compounds of regulatory interest.

The protocol will give the user guidance for instrument setup and calibration, as well as criteria to assess data quality. These criteria were established based on interlaboratory and intralaboratory evaluation of this protocol.

The QC requirements described in this document fall into three groups:

- QC requirements during the initialization process
- QC requirements during sample analysis
- QC requirements during ongoing calibration

Initialization Process

The initialization process includes the analysis of the system performance standard and three composite priority pollutant standards (concentrations 20, 100, 200, μg/mL). The system performance standard: (1) demonstrates ion abundance calibration criteria, via decafluorotriphenylphosphine (DFTPP) at 50 ng, (2) provides information regarding system linearity, and (3) demonstrates the ability to chromatograph acidic and basic compounds. The composite priority pollutant standards are analyzed only after the QC requirements for the system performance standard are met. Response

factors for the composite mixture of phenol, naphthalene, anthracene, chrysene, and benzo(a)pyrene are utilized as the principal indicator of data acceptability.

Sample Analysis

Sample analysis begins after the initialization criteria are met. During sample analysis, the absolute areas of the quantitation ions of the five internal standards (phenol-d_3, naphthalene-d_8, anthracene-d_{10}, chrysene-d_{12}, and benzo(a)pyrene-d_{12}) are monitored.

Ongoing Calibration

Ongoing calibration requires that after 8 hours of data acquisition, the system performance standard and a single level calibration standard are analyzed to verify system performance. One week after the first initialization procedure and after any maintenance is performed on the system, the initialization procedure must be repeated.

Results

This protocol was tested in an interlaboratory study; the precision/distribution of RF values observed is shown in Figure 1. When these interlaboratory RF values (as shown in Tables 1 and 1a) were compared to those obtained on a triple quadrupole mass spectrometer, 74 percent of the electron impact GC/MS response factors (RF) determined for 53 extractable priority pollutants were found to be within ±15 percent of values determined in the independent interlaboratory single quadrupole GC/MS study. The precision of RF determinations for 53 extractable priority pollutants (mean relative standard deviation 11.9 percent) was found to be similar to that previously observed for routine GC/MS multianalyte RF determinations.

Response factors may be viewed as constants to be utilized in the internal standard quantitative analysis of organic compounds by electron impact GC/MS in environmental analysis. For comparable injected weights, the response factor of an analyte is simply a ratio of the ion current "area" of analyte and internal standard at their respective quantitation m/z values. A series of multianalyte, multilevel response factor precision determinations can be considered as a measure of the relative sensitivity and stability of a given instrument and, hence, its quantitative capabilities. Response factor monitoring is an important mecha-

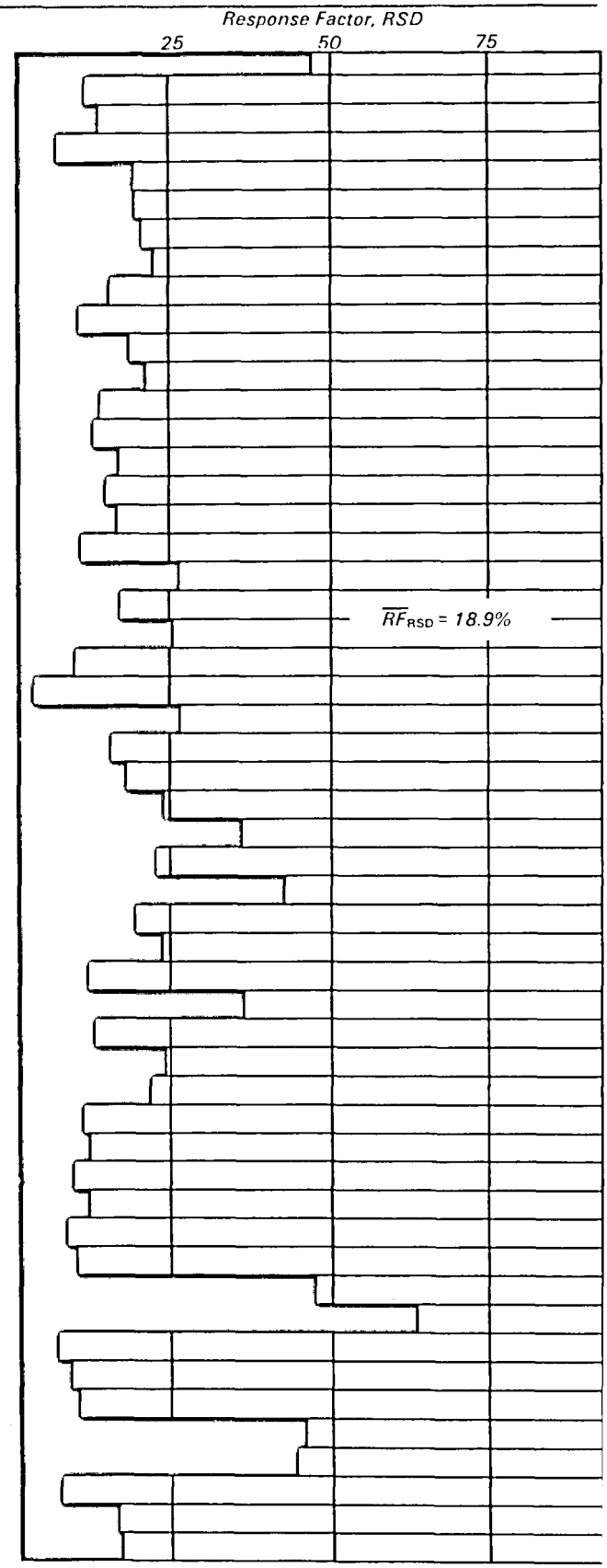

Figure 1. Interlaboratory (4 Lab) response factor relative standard deviation.

Table 1. Intralaboratory Response Factors of Semivolatile Priority Pollutants

Compound	Splitless Injection		On-Column Injection			
	RF[a]	RSD	$\overline{RF}$[a]	RSD	RRT[a]	RSD
N-Nitrosodimethylamine	0.72	24.5	---	---	---	---
Bis(2-chloroethyl)ether	0.96	3.0	1.078	11.4	0.988	0.2
2-Chlorophenol	0.73	4.0	1.001	9.2	0.994	0.2
Phenol	1.16	2.8	1.335	5.3	1.002	0.3
1,3-Dichlorobenzene	0.66	0.9	0.886	9.5	1.065	0.7
1,4-Dichlorobenzene	0.85	3.8	1.090	12.3	1.106	0.6
1,2-Dichlorobenzene	0.72	3.5	0.942	12.8	1.235	1.0
Bis(2-chloroisopropyl)ether	0.26	7.9	0.232	6.9	1.389	1.3
Hexachloroethane	0.35	8.2	0.428	9.0	1.455	1.5
N-Nitroso-di-n-propylamine	0.055	3.8	0.092	7.7	0.725	0.8
Nitrobenzene	0.18	0	0.251	4.4	0.750	0.4
Isophorone	0.89	1.7	0.810	14.7	0.852	0.6
2-Nitrophenol	0.23	6.7	0.326	1.4	0.872	0.3
2,4-Dimethylphenol	0.30	3.3	0.367	5.6	0.940	0.3
Bis(2-chloroethoxy)methane	0.53	1.9	0.541	3.8	0.964	0.2
2,4-Dichlorophenol	0.29	0	0.388	4.4	0.980	0.1
1,2,4-Trichlorobenzene	0.30	1.9	0.418	5.8	0.992	0.1
Naphthalene	1.01	6.5	1.089	19.2	1.008	0.1
Hexachlorobutadiene	0.12	0	0.188	5.4	1.093	0.3
4-Chloro-3-cresol	0.29	2.0	0.383	7.2	1.297	0.3
Hexachlorocyclopentadiene	0.15	7.5	0.259	6.9	1.377	0.3
2,4,6-Trichlorophenol	0.21	5.4	0.313	7.7	1.425	0.3
2-Chloronaphthalene	0.64	2.4	0.814	6.1	1.466	0.3
Acenaphthylene	0.88	4.3	0.994	6.5	1.626	0.3
Dimethyl phthalate	0.73	3.1	1.018	4.1	1.656	0.2
2,6-Dinitrotoluene	0.18	6.3	0.275	7.4	1.671	0.2
Acenaphthene	0.61	5.0	0.757	20.0	0.745	0.0
2,4-Dinitrophenol	0.083	38.3	0.166	16.8	0.768	0.2
2,4-Dinitrotoluene	0.23	11.1	0.325	2.5	0.795	0.2
4-Nitrophenol	0.18	8.3	0.207	17.0	0.806	0.1
Fluorene	0.77	7.8	0.866	15.6	0.833	0.1
4-Chlorophenyl phenylether	0.38	4.1	0.524	10.7	0.843	0.1
Diethyl Phthalate	0.82	4.6	1.018	14.9	0.849	0.1
4,6-Dinitro-2-cresol	0.14	16.9	0.219	11.0	0.863	0.3
Diphenylamine	0.52	4.0	0.587	8.0	0.870	0.1
Azobenzene	---	---	0.069	19.1	0.870	0.1
4-Bromophenyl phenyl ether	0.21	4.8	0.308	5.0	0.926	0.1
Hexachlorobenzene	0.24	4.2	0.339	5.7	0.941	0.1
Pentachlorophenol	0.14	7.1	0.205	10.4	0.931	0.1
Phenanthrene	1.06	1.4	1.221	7.2	0.996	0.1
Anthracene	1.07	8.0	1.045	25.0	1.003	0.1
Di-n-butyl phthalate	1.44	9.6	1.428	22.3	1.136	0.1
Fluoranthene	1.10	6.6	1.201	12.4	1.202	0.1
Pyrene	1.13	2.8	1.160	6.4	1.237	0.1
Benzidine	0.15	24.7	---	---	b	b
Butylbenzylphthalate	0.67	10.8	0.698	19.2	0.957	0.1
Benz(a)anthracene	1.04	2.4	1.043	5.0	0.998	0.1
Chrysene	1.02	6.1	0.878	21.1	1.002	0.1
3,3-Dichlorobenzidine	0.31	0	---	---	b	b
Bis(2-ethylhexyl)phthalate	1.07	3.9	1.012	21.7	1.037	0.1
Di-n-octyl phthalate	1.70	5.4	1.347	20.4	1.108	0.1
Benzo(j+k)fluoranthenes	---	---	---	---	b	b
Benzo(a)pyrene	0.88	2.3	0.961	21.3	1.002	0.1
Indeno(1,2,3-cd)pyrene	---	---	---	---	b	b
Dibenzo(a,h)anthracene	0.60	2.5	0.784	17.3	1.153	0.2
Benzo(ghi)perylene	0.65	8.6	0.815	15.3	1.185	0.3

[a]*Number of determinations is 3 for splitless injection and 7 for on-column injection.*
[b]*Compound not present in the standard.*

nism in establishing and maintaining control of multilaboratory programs that routinely employ GC/MS for the qualitative and quantitative analysis of organic compounds.

Table 1a. *Intralaboratory Response Factors of Pesticides*

Compound	Splitless Injection		On-Column Injection			
	RF[a]	RSD	$\overline{RF}$[a]	RSD	RRT[a]	RSD
Alpha-BHC	0.143	9.1	0.169	7.0	0.931	0.1
Gamma-BHC	0.154	13.7	0.269	9.2	0.982	0.1
Beta-BHC	0.188	28.4	0.247	24.3	1.024	0.1
Delta-BHC	0.103	6.2	0.127	5.0	1.024	0.1
Heptachlor	0.089	10.9	0.143	9.5	1.087	0.2
Aldrin	---	---	---	---	---	---
4,4'-DDE	0.243	14.8	0.246	8.7	0.883	0.1
Dieldrin	0.292	23.3	0.204	5.0	0.880	0.1
4,4'-DDD	0.458	12.1	0.476	6.0	0.923	0.1
4,4'-DDT	0.346	8.6	0.433	5.8	0.957	0.1
Beta Endosulfan	0.039	7.4	0.041	7.1	0.910	0.1
Endosulfan sulfate	---	---	0.089	12.0	---	---
Endrin	0.082	28.6	0.076	10.8	0.880	0.1
Alpha endosulfan	0.034	5.6	0.036	5.2	0.855	0.1
Heptachlor epoxide	0.059	6.2	0.077	8.5	1.196	0.2

[a]*Number of determinations is 3 for splitless injection and 7 for on-column injection.*

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The complete report, entitled "Fused Silica Capillary Column GC/MS Quality Control Protocol for the Determination of Semivolatile Priority Pollutants," (Order No. PB 84-224 674; Cost: $10.00, subject to change) will be available only from:
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