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Assessment of Sediment Contamination in Casco Bay Appendix C Trace Metal Analytical Results and Appendix D Standard Operating Procedures, 1992

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ASSESSMENT OF SEDIMENT CONTAMINATION IN CASCO BAY

Appendix C

Trace Metal Analytical Results

and

Appendix D

Standard Operating Procedures

prepared by

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prepared for the

CASCO BAY ESTUARY PROJECT

FINAL REPORT

August 1992

TECHNICAL REPORT #92-159

APPENDIX C

TRACE METAL ANALYTICAL RESULTS

INNER BAY REGION

NATIONAL ESTUARY PROGRAM - METAL DATA - CASCO BAY - 1991

	INNER BAY REGION									
INVEST#:	IB-1		IB-2		IB-3		IB-4		IB-5	
LABSAMNO:	910841		910843		910846		910847		910848	
ANALYTE:	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL
Bulk Parameters										
TOC (%):	3.0		3.3		3.2		2.1		2.0	
ORG NITROGEN (ppm):	2383		2278		2270		2390		1705	
% SAND:	6.3		11.5		6.8		4.3		16.0	
% SILT:	57.7		46.8		69.7		57.1		40.0	
% CLAY:	36.0		41.7		23.5		38.7		43.9	
Elemental Analyses										
UNITS:	ppm		ppm		ppm		ppm		ppm	
Ag:	0.57		0.46		0.39		0.27		0.20	
As:	12.80		9.90		13.70		11.40		11.00	
Cd:	0.564		0.524		0.574		0.571		0.325	
Cr:	82		85		79		86		74	
Cu:	48.40		29.60		29.50		24.30		20.50	
Hg:	0.269		0.271		0.264		0.274		0.094	
Ni:	34.0		32.1		31.7		34.6		27.5	
Pb:	55.6		49.9		48.5		41.5		38.1	
Se:	0.69		0.69		0.83		0.81		0.10	
Zn:	125		109		109		102		84	
UNITS:	%		%		%		%		%	
Fe:	3.61		3.38		3.37		3.49		2.96	

Data reported on a dry weight basis

LABNAME: GERG/TAMU DATE: 16-Apr-92 LAB APPROVAL: Terry L. Wade

NATIONAL ESTUARY PROGRAM - METAL DATA - CASCO BAY - 1991

	INNER BAY REGION				
INVEST#:	IB-6	IB-7	IB-8	IB-9	IB-10
LABSAMNO:	910849	910850	910851	910852	910853
ANALYTE:	CONC DB QUAL	CONC DB QUAL	CONC DB QUAL	CONC DB QUAL	CONC DB QUAL
Bulk Parameters					
TOC (%):	2.3	3.2	3.5	3.0	3.0
ORG NITROGEN (ppm):	1853	1930	2015	1705	1557
% SAND:	24.9	3.1	6.1	7.6	4.3
% SILT:	41.9	55.2	56.7	48.6	56.6
% CLAY:	33.3	41.8	37.3	43.8	39.1
Elemental Analyses					
UNITS:	ppm	ppm	ppm	ppm	ppm
Ag:	0.25	0.32	0.24	0.23	0.23
As:	16.00	15.70	14.20	12.90	13.50
Cd:	0.392	0.424	0.573	0.557	0.501
Cr:	80	91	84	89	87
Cu:	20.80	23.40	22.30	22.30	23.30
Hg:	0.195	0.234	0.168	0.173	0.170
Ni:	31.8	36.2	36.3	36.8	37.8
Pb:	41.2	42.1	35.3	36.2	36.0
Se:	0.85	1.11	0.90	1.00	0.95
Zn:	104	106	104	106	98
UNITS:	%	%	%	%	%
Fe:	3.22	3.78	3.45	3.78	3.69

Data reported on a dry weight basis

LABNAME: GERG/TAMU DATE: 16-Apr-92 LAB APPROVAL: Terry L. Wade

NATIONAL ESTUARY PROGRAM - METAL DATA - CASCO BAY - 1991

	INNER BAY REGION									
INVEST#:	SW-1		SW-2		SW-3		SW-4		SW-5	
LABSAMNO:	910806		910807		910808		910809		910811	
ANALYTE:	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL
Bulk Parameters										
TOC (%):	1.6		1.4		2.8		1.9		1.0	
ORG NITROGEN (ppm):	621		2841		2400		766		435	
% SAND:	45.3		32.6		31.1		68.6		48.8	
% SILT:	33.2		31.7		41.6		21.7		38.5	
% CLAY:	21.5		35.7		27.3		9.7		12.7	
Elemental Analyses										
UNITS:	ppm		ppm		ppm		ppm		ppm	
Ag:	0.46		0.57		0.78		0.19		0.12	
As:	9.11		11.30		9.42		1.62		2.99	
Cd:	0.488		0.478		0.908		0.213		0.245	
Cr:	50		56		75		31		44	
Cu:	25.10		28.10		34.50		7.92		8.69	
Hg:	0.264		0.392		0.424		0.097		0.062	
Ni:	29.2		23.1		27.9		7.8		12.8	
Pb:	55.5		70.3		75.6		32.0		27.5	
Se:	0.47		0.39		0.49		0.23		0.30	
Zn:	95		117		112		35		40	
UNITS:	%		%		%		%		%	
Fe:	2.28		2.59		2.88		0.98		1.59	

Data reported on a dry weight basis

LABNAME: GERG/TAMU DATE: 16-Apr-92 LAB APPROVAL: Terry L. Wade

NATIONAL ESTUARY PROGRAM - METAL DATA - CASCO BAY - 1991

	INNER BAY REGION
INVEST#:	SW-6
LABSAMNO:	910812
ANALYTE:	CONC DB QUAL
Bulk Parameters	
TOC (%):	2.9
ORG NITROGEN (ppm):	4161
% SAND:	32.3
% SILT:	38.9
% CLAY:	28.8
Elemental Analyses	
UNITS:	ppm
Ag:	0.13
As:	5.92
Cd:	0.435
Cr:	79
Cu:	18.90
Hg:	0.061
Ni:	27.2
Pb:	31.7
Se:	0.48
Zn:	78
UNITS:	%
Fe:	3.12

Data reported on a dry weight basis

LABNAME: GERG/TAMU DATE: 16-Apr-92 LAB APPROVAL: Terry L. Wade

WEST BAY REGION

NATIONAL ESTUARY PROGRAM - METAL DATA - CASCO BAY - 1991

	WEST BAY REGION									
INVEST#:	WB-6		WB-7		WB-8		WB-9		SW-7	
LABSAMNO:	910827		910828		910829		910830		910813	
ANALYTE:	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL
Bulk Parameters										
TOC (%):	2.1		1.8		1.3		2.2		0.8	
ORG NITROGEN (ppm):	1379		1853		1778		2496		1029	
% SAND:	4.6		34.2		46.0		13.6		49.1	
% SILT:	47.1		34.7		32.1		41.1		27.0	
% CLAY:	48.3		31.1		21.9		45.3		23.9	
Elemental Analyses										
UNITS:	ppm		ppm		ppm		ppm		ppm	
Ag:	0.11		0.11		0.13		0.36		0.07	
As:	13.90		13.80		10.60		13.00		4.76	
Cd:	0.088		0.312		0.293		0.302		0.155	
Cr:	82		72		66		93		46	
Cu:	20.30		17.70		15.20		19.50		9.77	
Hg:	0.057		0.071		0.077		0.087		0.032	
Ni:	33.4		29.6		23.5		30.8		14.4	
Pb:	31.7		27.1		26.8		31.9		24.7	
Se:	0.33		0.55		0.62		1.12		0.40	
Zn:	92		80		68		93		46	
UNITS:	%		%		%		%		%	
Fe:	4.04		3.26		2.88		3.57		1.94	

Data reported on a dry weight basis

LABNAME: GERG/TAMU DATE: 16-Apr-92 LAB APPROVAL: Terry L. Wade

NATIONAL ESTUARY PROGRAM - METAL DATA - CASCO BAY - 1991

	WEST BAY REGION									
INVEST#:	WB-1		WB-2		WB-3		WB-4		WB-5	
LABSAMNO:	910822		910823		910824		910825		910826	
ANALYTE:	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL
Bulk Parameters										
TOC (%):	2.7		2.0		0.9		3.1		2.4	
ORG NITROGEN (ppm):	3096		2606		1326		3353		1050	
% SAND:	9.9		6.0		38.7		3.5		5.1	
% SILT:	48.9		55.1		35.1		59.2		49.6	
% CLAY:	41.1		39.0		26.3		37.3		42.3	
Elemental Analyses										
UNITS:	ppm		ppm		ppm		ppm		ppm	
Ag:	0.15		0.17		0.11		0.17		0.15	
As:	13.00		11.80		8.34		12.50		15.00	
Cd:	0.430		0.358		0.258		0.444		0.529	
Cr:	71		81		60		78		85	
Cu:	17.10		20.30		13.60		19.80		21.50	
Hg:	0.087		0.076		0.031		0.082		0.069	
Ni:	30.2		34.0		25.9		34.3		35.0	
Pb:	28.4		29.7		20.5		28.6		27.4	
Se:	0.96		0.72		0.52		0.84		0.74	
Zn:	93		92		69		94		140	
UNITS:	%		%		%		%		%	
Fe:	3.29		3.57		2.89		3.63		4.05	

Data reported on a dry weight basis

LABNAME: GERG/TAMU DATE: 16-Apr-92 LAB APPROVAL: Terry L. Wade

NATIONAL ESTUARY PROGRAM - METAL DATA - CASCO BAY - 1991

	WEST BAY REGION									
INVEST#:	SW-8		SW-9		SW-10		SW-11		SW-12	
LABSAMNO:	910814		910815		910816		910817		910818	
ANALYTE:	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL
Bulk Parameters										
TOC (%):	0.7		1.7		2.7		2.1		2.0	
ORG NITROGEN (ppm):	501		3095		2401		3094		2200	
% SAND:	68.2		6.1		19.5		9.5		49.1	
% SILT:	24.1		51.1		42.0		43.7		33.6	
% CLAY:	7.7		42.8		38.6		46.8		17.3	
Elemental Analyses										
UNITS:	ppm		ppm		ppm		ppm		ppm	
Ag:	0.09		0.17		0.16		0.16		0.25	
As:	5.04		9.90		10.50		11.30		8.41	
Cd:	0.150		0.400		0.486		0.239		0.355	
Cr:	35		87		76		88		56	
Cu:	6.98		20.90		17.40		26.20		18.90	
Hg:	0.019		0.037		0.037		0.096		0.048	
Ni:	9.7		30.6		24.5		31.7		23.6	
Pb:	20.5		25.5		22.2		37.6		29.4	
Se:	0.12		0.52		0.45		0.53		0.50	
Zn:	34		87		73		95		71	
UNITS:	%		%		%		%		%	
Fe:	1.50		3.82		3.42		3.89		2.64	

Data reported on a dry weight basis

LABNAME: GERG/TAMU DATE: 16-Apr-92 LAB APPROVAL: Terry L. Wade

NATIONAL ESTUARY PROGRAM - METAL DATA - CASCO BAY - 1991

	WEST BAY REGION
INVEST#:	SW-13
LABSAMNO:	910819
ANALYTE:	CONC DB QUAL
Bulk Parameters	
TOC (%):	1.4
ORG NITROGEN (ppm):	2611
% SAND:	3.2
% SILT:	50.9
% CLAY:	45.9
Elemental Analyses	
UNITS:	ppm
Ag:	0.15
As:	19.60
Cd:	0.125
Cr:	100
Cu:	22.50
Hg:	0.073
Ni:	38.6
Pb:	31.5
Se:	0.52
Zn:	101
UNITS:	%
Fe:	4.61

Data reported on a dry weight basis

LABNAME: GERG/TAMU DATE: 16-Apr-92 LAB APPROVAL: Terry L. Wade

EAST BAY REGION

NATIONAL ESTUARY PROGRAM - METAL DATA - CASCO BAY - 1991

	EAST BAY REGION									
INVEST#:	EB-1		EB-2		EB-3		EB-4		EB-5	
LABSAMNO:	910831		910832		910833		910840		910834	
ANALYTE:	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL
Bulk Parameters										
TOC (%):	1.5		2.3		2.4		0.8		3.9	
ORG NITROGEN (ppm):	1025		762		2392		1087		4515	
% SAND:	34.7		33.2		25.1		62.3		16.5	
% SILT:	26.0		29.4		42.1		21.0		41.6	
% CLAY:	39.4		37.4		32.9		16.7		41.9	
Elemental Analyses										
UNITS:	ppm		ppm		ppm		ppm		ppm	
Ag:	0.11		0.11		0.19		0.10		0.23	
As:	9.20		6.58		12.70		8.33		17.00	
Cd:	0.127		0.175		0.431		0.076		0.794	
Cr:	71		84		92		81		96	
Cu:	13.20		9.94		19.70		12.40		24.80	
Hg:	0.059		0.077		0.112		0.058		0.176	
Ni:	22.3		22.9		28.4		19.8		34.1	
Pb:	26.2		25.8		33.2		23.3		37.0	
Se:	0.48		0.38		0.68		0.37		1.11	
Zn:	62		68		87		59		101	
UNITS:	%		%		%		%		%	
Fe:	2.63		2.47		3.06		2.64		3.54	

Data reported on a dry weight basis

LABNAME: GERG/TAMU DATE: 16-Apr-92 LAB APPROVAL: Terry L. Wade

NATIONAL ESTUARY PROGRAM - METAL DATA - CASCO BAY - 1991

	EAST BAY REGION									
INVEST#:	EB-6		EB-7		EB-8		EB-9		EB-10	
LABSAMNO:	910835		910836		910837		910838		910839	
ANALYTE:	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL
Bulk Parameters										
TOC (%):	3.7		3.5		3.6		4.6		1.1	
ORG NITROGEN (ppm):	4701		2961		3505		2719		944	
% SAND:	20.5		6.0		25.6		21.7		45.8	
% SILT:	46.3		52.0		33.7		37.4		23.4	
% CLAY:	33.3		42.0		40.8		40.8		30.7	
Elemental Analyses										
UNITS:	ppm		ppm		ppm		ppm		ppm	
Ag:	0.29		0.20		0.23		0.19		0.08	
As:	16.20		15.70		15.30		13.90		6.03	
Cd:	1.320		0.608		0.720		0.401		0.121	
Cr:	99		105		103		99		82	
Cu:	27.90		25.20		24.60		20.00		9.94	
Hg:	0.137		0.153		0.181		0.148		0.069	
Ni:	35.2		38.4		32.9		29.5		19.0	
Pb:	33.2		31.6		34.1		32.1		20.6	
Se:	1.11		0.97		0.82		0.85		0.27	
Zn:	105		100		97		92		56	
UNITS:	%		%		%		%		%	
Fe:	3.58		3.88		3.70		3.30		2.56	

Data reported on a dry weight basis

LABNAME: GERG/TAMU DATE: 16-Apr-92 LAB APPROVAL: Terry L. Wade

NATIONAL ESTUARY PROGRAM - METAL DATA - CASCO BAY - 1991

	EAST BAY REGION			
INVEST#:	SW-14		SW-15	
LABSAMNO:	910820		910821	
ANALYTE:	CONC	DB QUAL	CONC	DB QUAL
Bulk Parameters				
TOC (%):	2.5		1.2	
ORG NITROGEN (ppm):	2206		764	
% SAND:	30.7		71.0	
% SILT:	36.2		23.2	
% CLAY:	33.1		5.8	
Elemental Analyses				
UNITS:	ppm		ppm	
Ag:	0.16		0.08	
As:	10.90		3.20	
Cd:	0.414		0.192	
Cr:	77		29	
Cu:	17.00		5.59	
Hg:	0.082		0.048	
Ni:	24.9		8.4	
Pb:	24.3		13.6	
Se:	0.53		0.40	
Zn:	75		28	
UNITS:	%		%	
Fe:	3.20		1.21	

Data reported on a dry weight basis

LABNAME: GERG/TAMU DATE: 16-Apr-92 LAB APPROVAL: Terry L. Wade

CAPE SMALL REGION

NATIONAL ESTUARY PROGRAM - METAL DATA - CASCO BAY - 1991

	CAPE SMALL STATIONS				
INVEST#:	CS-1	CS-2	CS-3	CS-4	CS-5
LABSAMNO:	910799	910800	910801	910802	910803
ANALYTE:	CONC DB QUAL	CONC DB QUAL	CONC DB QUAL	CONC DB QUAL	CONC DB QUAL
Bulk Parameters					
TOC (%):	0.2	0.2	< 0.1	2.7	0.3
ORG NITROGEN (ppm):	84	129	291	1181	298
% SAND:	88.1	87.1	84.1	29.9	82.4
% SILT:	10.7	10.6	13.0	32.6	12.7
% CLAY:	1.2	2.4	2.9	37.5	4.9
Elemental Analyses					
UNITS:	ppm	ppm	ppm	ppm	ppm
Ag:	0.05	0.07	0.06	0.20	0.09
As:	5.72	5.47	9.42	13.70	5.03
Cd:	0.071	0.060	0.053	0.208	0.036
Cr:	61	52	50	93	67
Cu:	3.18	4.43	2.52	21.60	5.31
Hg:	< 0.006 J	0.019	0.008 J	0.190	0.031
Ni:	16.1	13.9	14.2	30.6	16.1
Pb:	14.1	17.8	17.6	32.4	20.0
Se:	0.34	< 0.07 J	< 0.07 J	0.65	0.13 J
Zn:	39	34	35	88	38
UNITS:	%	%	%	%	%
Fe:	2.45	1.86	2.22	3.28	2.22

Data reported on a dry weight basis

LABNAME: GERG/TAMU DATE: 16-Apr-92 LAB APPROVAL: Terry J. Wade

NATIONAL ESTUARY PROGRAM - METAL DATA - CASCO BAY - 1991

	CAPE SMALL STATIONS			
INVEST#:	CS-6		CS-7	
LABSAMNO:	910804		910805	
ANALYTE:	CONC	DB QUAL	CONC	DB QUAL
Bulk Parameters				
TOC (%):	0.7		< 0.1	
ORG NITROGEN (ppm):	589		71	
% SAND:	65.9		89.5	
% SILT:	21.6		10.2	
% CLAY:	12.5		0.3	
Elemental Analyses				
UNITS:	ppm		ppm	
Ag:	0.07		0.05	
As:	5.15		12.40	
Cd:	0.051		0.069	
Cr:	71		37	
Cu:	6.00		3.09	
Hg:	0.046		< 0.006	J
Ni:	15.2		12.9	
Pb:	20.8		17.1	
Se:	0.31		0.13	J
Zn:	46		31	
UNITS:	%		%	
Fe:	2.37		1.92	

Data reported on a dry weight basis

LABNAME: GERG/TAMU DATE: 16-Apr-92 LAB APPROVAL: Terry L. Wade

OUTER BAY REGION

NATIONAL ESTUARY PROGRAM - METAL DATA - CASCO BAY - 1991

	OUTER BAY REGION									
INVEST#:	OB-1		OB-2		OB-3		OB-4		OB-5	
LABSAMNO:	910785		910786		910787		910788		910789	
ANALYTE:	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL
Bulk Parameters										
TOC (%):	2.1		1.4		2.7		1.6		2.1	
ORG NITROGEN (ppm):	1269		1213		1638		1268		1571	
% SAND:	4.2		42.5		10.9		22.7		29.5	
% SILT:	58.3		35.1		57.0		42.9		37.1	
% CLAY:	37.6		22.4		32.1		34.5		33.4	
Elemental Analyses										
UNITS:	ppm		ppm		ppm		ppm		ppm	
Ag:	0.14		0.12		0.20		0.17		0.15	
As:	11.60		20.50		16.40		12.00		9.89	
Cd:	0.118		0.133		0.327		0.226		0.200	
Cr:	88		89		93		77		85	
Cu:	16.00		17.40		26.20		14.90		16.30	
Hg:	0.065		0.058		0.141		0.104		0.085	
Ni:	35.3		32.4		39.8		24.4		33.3	
Pb:	27.7		37.7		40.7		33.1		34.7	
Se:	0.78		0.99		0.78		0.38		0.89	
Zn:	88		92		109		75		81	
UNITS:	%		%		%		%		%	
Fe:	3.87		3.96		4.21		3.11		3.24	

Data reported on a dry weight basis

LABNAME: GERG/TAMU DATE: 16-Apr-92 LAB APPROVAL: Terry L. Wade

NATIONAL ESTUARY PROGRAM - METAL DATA - CASCO BAY - 1991

	OUTER BAY REGION									
INVEST#:	OB-6		OB-7		OB-8		OB-9		OB-10	
LABSAMNO:	910790		910791		910792		910793		910794	
ANALYTE:	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL
Bulk Parameters										
TOC (%):	2.2		1.1		1.6		2.6		2.6	
ORG NITROGEN (ppm):	1149		2024		1783		2610		2199	
% SAND:	26.4		37.7		33.1		17.0		31.8	
% SILT:	43.0		35.0		39.4		49.9		44.3	
% CLAY:	30.6		27.4		27.5		33.2		23.9	
Elemental Analyses										
UNITS:	ppm		ppm		ppm		ppm		ppm	
Ag:	0.26		0.16		0.14		0.17		0.14	
As:	14.40		11.90		11.60		13.20		10.70	
Cd:	0.592		0.245		0.176		0.174		0.156	
Cr:	83		71		77		93		84	
Cu:	17.80		14.10		13.60		17.90		15.40	
Hg:	0.106		0.113		0.087		0.113		0.081	
Ni:	24.6		24.7		28.8		33.1		25.6	
Pb:	32.8		35.8		35.7		38.3		33.8	
Se:	0.81		0.72		0.75		0.57		0.47	
Zn:	86		75		76		91		82	
UNITS:	%		%		%		%		%	
Fe:	3.24		2.80		3.06		3.54		3.24	

Data reported on a dry weight basis

LABNAME: GERG/TAMU DATE: 16-Apr-92 LAB APPROVAL: Terry L. Wade

NATIONAL ESTUARY PROGRAM - METAL DATA - CASCO BAY - 1991

	OUTER BAY REGION							
INVEST#:	OB-11		OB-12		OB-13		OB-15	
LABSAMNO:	910795		910796		910797		910798	
ANALYTE:	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL	CONC	DB QUAL
Bulk Parameters								
TOC (%):	1.4		2.8		2.3		2.1	
ORG NITROGEN (ppm):	1443		2603		2106		3367	
% SAND:	45.6		21.9		24.2		32.4	
% SILT:	31.7		46.9		44.3		34.6	
% CLAY:	22.7		31.2		31.6		33.0	
Elemental Analyses								
UNITS:	ppm		ppm		ppm		ppm	
Ag:	0.10		0.19		0.15		0.16	
As:	5.20		12.80		10.80		7.83	
Cd:	0.168		0.434		0.268		0.155	
Cr:	43		86		75		82	
Cu:	6.94		19.30		15.60		14.70	
Hg:	0.049		0.118		0.082		0.102	
Ni:	14.5		34.0		27.7		27.2	
Pb:	25.5		35.1		30.6		29.3	
Se:	0.31		0.99		0.44		0.62	
Zn:	43		92		82		75	
UNITS:	%		%		%		%	
Fe:	1.70		3.41		3.20		2.81	

Data reported on a dry weight basis

LABNAME: GERG/TAMU DATE: 16-Apr-92 LAB APPROVAL: Terry L. Wade

APPENDIX D

STANDARD OPERATING PROCEDURES

EXTRACTION OF SEDIMENTS FOR TRACE ORGANIC ANALYSIS

1.0 INTRODUCTION

Assessment of the environmental levels of aromatic and chlorinated hydrocarbons (pesticides and PCBs) requires their measurement in sediments at trace levels (parts per billion to parts per trillion).

Ten (10) grams (dry weight) of freeze-dried sediment is Soxhlet extracted with methylene chloride, the extract is concentrated and purified using silica gel/alumina column purification to remove matrix interferences. The purified extract is then submitted for analysis of aromatic and chlorinated hydrocarbons by GERG SOP-ST03 and ST04, respectively.

2.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

2.1 Sample Collection

Sediment is collected in precleaned glass jars and frozen (-20°C) in the field.

2.2 Sample Preservation and Storage

Sediment samples are shipped frozen to the laboratory and stored at -20°C until analysis. After subsampling, archive excess sample is archived at -20°C in the dark. Extracts are stored in the dark at or below 4°C.

3.0 INTERFERENCES

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to false positives during instrumental analysis. All materials used in this method are routinely demonstrated to be free from interferences by processing procedural blanks identical to samples (one blank per 20 samples or each batch whichever is more frequent).

Matrix interferences result from co-extraction of compounds other than the analytes of interest. Elemental sulfur and naturally occurring lipids can cause interferences in the analysis of sediment extracts. Silica gel/alumina cleanup with activated copper is used to purify the sample prior to analysis.

4.0 APPARATUS AND MATERIALS

4.1 Labware and Apparatus

Clean glassware by detergent (Micro cleaning solution) washing with water and rinsing with tap water. The glassware is then combusted in a muffle furnace at 400°C for at least 4 hours. Solvent rinses of acetone followed by methylene chloride may be substituted for the muffle furnace heating when determined to be appropriate by the analyst. After drying and cooling, seal and store glassware in a clean environment to prevent the accumulation of dust or other contaminants. Stored glassware is maintained capped with combusted aluminum foil.

The following labware and equipment is needed to perform the sediment extraction and purification procedure:

Glass Jars: 250 mL or 500 mL glass jars, or other suitable containers.

Vials: 1 mL to 7 mL glass vials with Teflon-lined caps.

Glass Funnels

Flat Bottom Flasks: 250 and 500 mL.

Soxhlet Extractor Flasks: 40 mm ID and condensor.

Thimbles: Alundum, medium or coarse, 44 mL round bottom.

Concentrator Tube: Kuderna-Danish - 25 mL, graduated. Ground glass stoppers are used to prevent evaporation of extracts.

Snyder Column: Kuderna-Danish - 3-ball column.

Micro Reaction Vessels: 2.0 mL or 1.0 mL autosampler vials with crimp cap septa.

Chromatographic Column: 300 mm x 10 mm ID, with Pyrex glass wool at bottom and Teflon stopcock.

Analytical Balance: Capable of weighing to 0.0001 mg.

Analytical Balance: Capable of weighing to 0.1 g.

Water Bath: Heated to 60°-70°C.

Teflon Boiling Chips: Solvent extracted.

Syringes: 10 or 25 µl.

Disposable Glass Pasteur Pipets: 1 mL.

Pyrex Glass Wool: Combusted at 400°C for 4 h.

Nitrogen Gas Evaporation Unit

Note: Volumetric glassware for sample measurement or introduction of internal standards must be calibrated.

4.2 Reagents

Reagent Water: Reagent water contains no analytes above the method detection limit.

Sand: Combusted at 400°C for 4 h.

Sodium Sulfate: (ACS) Granular, anhydrous (purified by heating at 400°C for 4 h in a shallow tray or other suitable method).

Solvents: Hexane, methylene chloride (pesticide quality or equivalent).

Alumina: Neutral 80-325 MCB chromatographic grade or equivalent. Dry alumina overnight at 120°C prior to use.

Silica: Grade 923, 100-200 mesh Aldrich 21,447-7 or equivalent. Combusted at 400°C for 4 h and stored at 170°C before use.

Activated Copper Powder

Surrogate Spiking Solutions: Refer to GERG SOP-ST03 and ST04 for preparation of appropriate surrogate spiking solution for aromatic and chlorinated hydrocarbon analysis.

Matrix Spike Standard: Refer to GERG SOP-ST03 and ST04 for preparation of appropriate matrix spiking solution for aromatic and chlorinated hydrocarbon analysis.

Internal Standard Solution: Refer to GERG SOP-ST03 and ST04 for preparation of appropriate internal standard spiking solution for aromatic and chlorinated hydrocarbon analysis.

5.0 PROCEDURE

5.1 Sample Preparation

5.1.1 Weigh, freeze-dry, and reweigh a subsample to obtain percent moisture. Also freeze-dry the rest of the sample, unless a frozen archive sample is needed. Homogenize the freeze-dried sample by mortar and pestle, remove an aliquot (10g), and accurately weigh.

5.1.2 Add 10 g (dry weight) of the sample to an extraction thimble. Add 150 mL of methylene chloride to the extraction flask containing 1 or 2 boiling chips. Wet the sediment in the thimble with CH_2Cl_2.

5.1.3 Add surrogates to the sediment in the thimble. Spike with aromatic and chlorinated hydrocarbon surrogates as directed in GERG SOP-ST03 and ST04.

5.1.4 Attach the 250 mL flat bottom flask and extract the sample for 4 to 8 hours. Recycling should occur every 4 minutes.

5.1.5 If necessary, filter and dry the extract with glass wool and sodium sulfate.

5.1.6 Concentrate the extract by Kuderna-Danish techniques to 4-5 mL. Transfer to a 25 mL concentrator tube. Rinse the flat bottom flask with 5 mL of hexane and transfer the rinse to the concentrator tube. Concentrate to 1.0 mL.

5.2 Silica /Alumina Column Cleanup

5.2.1 Fill the column with hexane. Place a plug of glass wool and 1 cm of combusted sand in the glass chromatographic column.

5.2.2 Slurry pack 10 g of alumina (deactivated 1% with water) in CH_2Cl_2 into the column. Allow the alumina to settle.

5.2.3 Slurry pack 20 g of silica gel (deactivated 5% with water) in CH_2Cl_2 into the column. Allow to settle. Add 1 cm of combusted sand and 1-2 cm of activated copper on top of the packed column. Allow CH_2Cl_2 to drain to the top of the copper.

5.2.4 Add 50 mL of pentane to the column and drain to the top of the copper.

5.2.5 Place a 500 mL flat bottom flask under the column. Using hexane transfer the sample extract to the column. Drain column to the top of the copper. Rinse concentrator tube twice with 1 mL of 50:50 pentane:methylene chloride, add it to the column and drain the column to the copper layer. Add 200 mL of 50:50/pentane:CH_2Cl_2 to the column, elute at 1 mL/min and collect the effluent. This fraction contains the aromatic and chlorinated hydrocarbons.

5.2.6 Concentrate the extract as described in Section 5.1.6.

5.3 Preparation for Instrumental Analysis

5.3.1 Concentrate the extract to 1 mL in hexane for aromatic and chlorinated hydrocarbon analysis and analyze per GERG SOP-ST03 and ST04, respectively.

6.0 QUALITY CONTROL

Quality control samples are processed in a manner identical to actual samples.

6.1 Run a method blank with every 20 samples, or with every sample set, whichever is more frequent. Blank levels should be no more than 3x the method detection limit (MDL). If blank levels for any component are above 3x MDL, samples analyzed in that sample set should be re-extracted and reanalyzed. If insufficient sample is available for extraction, the data is reported and appropriately qualified.

6.2 Run matrix spike/matrix spike duplicate (MS/MSD) samples with every 20 samples, or with every sample set, whichever is more frequent. The appropriate spiking level is 3 to 10x the MDL.

6.3 Spike surrogate materials into every sample and QC sample. The appropriate spiking level is 3 to 10x the MDL.

6.4 Surrogate and matrix spike recovery acceptance criteria are described in detail in GERG SOP-ST03 and ST04.

6.5 Reference Materials: When available sediment reference material with certified aromatic and chlorinated hydrocarbons concentrations are analyzed with each sample batch (~20 samples) to establish control charts for these analyses.

7.0 REPORTING AND PERFORMANCE CRITERIA

7.1 Reporting units are ng/g .

7.2 The minimum performance standard for each analyte is described under the appropriate instrument SOP.

Note: The effective minimum performance standard can be adjusted by decreasing final sample volume, increasing sample amount and/or increasing volume injected.

8.0 EXAMPLE FORMS

8.1 Sediment Sample, Preparation, Extraction and Purification Form.

NOAA
Status & Trends

SEDIMENT SAMPLES
Sample Preparation
Sample Extraction / Purification

P_____

File#	Designator & Station	Wet Wt. (g)	Dry Wt. (%)	Dry Wt. (g)	Comments:
1	K ___				
2	K ___				
3	K ___				
4	K ___				
5	K ___				
6	K ___				
7	K ___				
8	K ___				
9	K ___				
10	K ___				
11	K ___				
12	K ___				
13	K ___				
14	K ___				
15	K ___				
16	K ___				
17	K ___				
18	K ___				
19	K ___				
20	K ___				

QA DOCUMENTATION
% MOISTURE WT
SAMPLE WT
EXTRACTION
K-D CONCENTRATION
COLUMN CHROMA.
K-D CONCENTRATION
• TO ANALYTICAL LAB
• Rcd ANALYTICAL LAB
• INTERNAL STD ADD.

Blanks & Spikes

File#	Designator & Station	Wet Wt. (g)	Dry Wt. (%)	Dry Wt. (g)	Comments:
21	Q ___				
22	Q ___				
23	Q ___				

DB189

NOAA
Status & Trends

SEDIMENT SAMPLES
Sample Preparation
Sample Extraction / Purification

P_____

	File#	Designator & Station	Wet Wt. (g)	Dry Wt. (%)	Dry Wt. (g)	Comments:
1	K ___					
2	K ___					
3	K ___					
4	K ___					
5	K ___					
6	K ___					
7	K ___					
8	K ___					
9	K ___					
10	K ___					
11	K ___					
12	K ___					
13	K ___					
14	K ___					
15	K ___					
16	K ___					
17	K ___					
18	K ___					
19	K ___					
20	K ___					

QA DOCUMENTATION
% MOISTURE WT
SAMPLE WT
EXTRACTION
K-D CONCENTRATION
COLUMN CHROMA.
K-D CONCENTRATION
• TO ANALYTICAL LAB
• Rcd ANALYTICAL LAB
• INTERNAL STD ADD.

Blanks & Spikes

	File#	Designator & Station	Wet Wt. (g)	Dry Wt. (%)	Dry Wt. (g)	Comments:
21	Q ___					
22	Q ___					
23	Q ___					

DBMS9

QUANTITATIVE DETERMINATION OF POLYNUCLEAR AROMATIC HYDROCARBONS BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY (GC/MS) - SELECTED ION MONITORING (SIM) MODE

1.0 INTRODUCTION

The quantitative method described in this document determines polynuclear aromatic hydrocarbons (PAH) and their alkylated homologues in extracts of biological tissues and sediments. Quantitation is performed by gas chromatography mass spectrometry (GC/MS) in the selected ion monitoring mode (SIM). Target analytes are listed in Table 1.

Extracts should be prepared as described in GERG SOP's ST01 and ST02 for biological tissues and sediments, respectively.

Sample collection, preservation, storage and holding times are discussed under the analytical procedures for sample extraction and purification.

2.0 APPARATUS AND MATERIALS

2.1 Gas Chromatograph/Mass Spectrometer

The analytical systems includes a temperature programmable gas chromatograph (Hewlett-Packard 5890A, or equivalent) and all accessories including syringes, analytical columns, and gases. The injection port should be designed for split or splitless injection, though routine analyses are operated in a splitless mode. A 30-m long x 0.32-mm I.D. fused silica capillary column with DB-5 bonded phase (J&W Scientific) should be used. The autosampler should be capable of making 1-4 µL injections.

The mass spectrometer (HP MSD) operates at 70 eV electron energy in the electron impact ionization mode and is tuned to maximize the sensitivity of the instrument based on manufacturer specifications. The GC capillary column is directly inserted into the ion source of the mass spectrometer.

The mass spectrometer computer system allows continuous acquisition and storage of all data during the chromatographic analyses. Computer software allows display of any GC/MS data file for ions of a specific mass and plotting ion abundances versus time or scan number.

Table 1. Target Compounds.

Compounds	I.S. Reference	Surrogate Reference	Compounds	I.S. Reference	Surrogate Reference
Naphthalene	A	1	Fluoranthene	B	3
C_1-Naphthalenes	A	1	C_1-Fluoranthenes[a]	B	3
C_2-Naphthalenes	A	2			
C_3-Naphthalenes	A	2	Pyrene	B	3
C_4-Naphthalenes[a]	A	2	C_1-Pyrene	B	3
Biphenyl	A	2	Benzo[a]anthracene	B	4
Acenaphthylene	A	2			
			Chrysene	B	4
Acenaphthene	A	2	C_1-Chrysene[a]	B	4
			C_2-Chrysene[a]	B	4
Fluorene	A	2	C_3-Chrysene[a]	B	4
C_1-Fluorenes[a]	A	2	C_4-Chrysene[a]	B	4
C_2-Fluorenes[a]	A	2			
C_3-Fluorenes[a]	A	2	Benzo[b]fluoranthene	B	4
			Benzo[k]fluoranthene	B	4
Dibenzothiophene	A	3	Benzo[e]pyrene	B	4
C_1-Dibenzothiophenes[a]	A	3	Benzo[a]pyrene	B	4
C_2-Dibenzothiophenes[a]	A	3	Perylene	B	4
C_3-Dibenzothiophenes[a]	A	3	Indeno[1,2,3-c,d]pyrene	B	4
			Dibenzo[a,h]anthracene	B	4
Phenanthrene	A	3	Benzo[g,h,i]perylene	B	4
C_1-Phenanthrenes	A	3			
C_2-Phenanthrenes[a]	A	3	Specific Isomers		
C_3-Phenanthrenes[a]	A	3			
C_4-Phenanthrenes[a]	A	3	1-methylnaphthalene	A	1
			2-methylnaphthalene	A	1
Anthracene	A	3	2,6-dimethylnaphthalene	A	2
C_1-Anthracenes[a]	A	3	2,3,5-trimethylnapthalene	A	2
C_2-Anthracenes[a]	A	3	1-methylphenanthrene	A	3
C_3-Anthracenes[a]	A	3			
C_4-Anthracenes[a]	A	3	Surrogates		
Internal Standards			Naphthalene-d_8	(1)	
			Acenaphthene-d_{10}	(2)	
Fluorene-d_{10}	(A)		Phenanthrene-d_{10}	(3)	
Benzo (a) pyrene-d_{12}	(B)		Chrysene-d_{12}	(4)	
			Perylene-d_{12}	(5)	

[a]Alkylated homologues not included in the calibration solution.
NOTE: Alkylated phenanthrenes and anthracenes, and alkylated fluoranthenes and pyrenes are quantified together as total alkylated (Cx) phenanthrene/anthracenes and total alkylated (Cx) fluoranthenes/pyrenes. Only the parent compounds and specific isomers are reported as individual compounds.

3.0 REAGENTS

3.1 Surrogate Spiking Solution

A surrogate solution is made by weighing appropriate aliquots of pure compounds into a volumetric flask and diluting to volume with methylene chloride [or by purchase of a certified standard (NIST) or equivalent]. Surrogates are added to the samples prior to extraction at a concentration of ~10x the MDL. If higher concentrations of oil are expected, the surrogate concentration can be increased appropriately.

The compounds in the surrogate solution are naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}. The surrogate solution provides a spike where approximately 100 µl of solution gives a final concentration of 40 ng/mL in the extract regardless of matrix. Sample analyte concentrations can be reported as corrected or uncorrected for surrogate recoveries.

3.2 Internal Standard Solutions

A solution containing each internal standard at 4 µg/mL is prepared by weight a certified standard (NIST or equivalent) into a volumetric flask and diluting to volume with methylene chloride. The internal standards are resolved from all, but elute in close proximity to, the analytes of interest. The internal standards are fluorene-d_{10}, and benzo(a)pyrene-d_{12}. Sufficient solvent is added to the extract prior to analysis to give a final concentration of the internal standard of 40 ng/mL.

3.3 Matrix Recovery Standard Spiking Solution

A solution containing 2 to 5-ring PAH compounds is used to fortify matrix spike samples (Table 2). A certified solution purchased from a commercial vendor (NIST SRM 1491) is diluted to the appropriate working concentration. The spiking solution is added to give a final concentration of ~10x the MDL. For higher concentrations of oil the matrix spike is appropriately increased.

Table 2. PAH Matrix Spike Compounds in CH_2Cl_2.

Compound	Spiking Solution Concentration (µg/g)
Naphthalene	10.30 ± 0.10
1-Methylnaphthalene	12.4 ± 0.5
2-Methylnaphthalene	11.8 ± 0.04
Biphenyl	10.46 ± 0.04
2,6-Dimethylnaphthalene	10.8 ± 0.4
Acenaphthylene	10.40 ± 0.07
Acenaphthene	10.89 ± 0.15
2,3,5-Trimethylnaphthalene	9.9 ± 0.4
Fluorene	10.87 ± 0.08
Dibenzothiphene	10.00 ± 0.01*
Phenanthrene	10.48 ± 0.07
Anthracene	11.69 ± 0.06
1-Methylphenanthrene	10.4 ± 0.3
Fluoranthene	8.84 ± 0.06
Pyrene	8.81 ± 0.08
Benz[a]anthracene	7.85 ± 0.05
Chrysene	10.50 ± 0.06
Benzo[b]fluoranthene	7.85 ± 0.05
Benzo[k]fluoranthene	8.33 ± 0.12
Benzo[e]pyrene	8.40 ± 0.04
Benzo[a]pyrene	10.14 ± 0.09
Perylene	10.65 ± 0.06
Indeno[1,2,3-cd]pyrene	9.40 ± 0.07
Dibenz[a,h]anthracene	7.74 ± 0.18
Benzo[ghi]perylene	7.90 ± 0.13

*Added to NIST SRM 1491

4.0 GC/MS CALIBRATIONS

A five-point response factor calibration curve is established demonstrating the linear range of the detector. The recommended standard concentrations are 20, 100, 250, 500, 1000 ng/mL. The percent relative standard deviation for all calibrated analytes must not exceed ±15 percent with an $R > 0.99$ with a 1st degree fit of the data.

After every 6-8 samples, the mass spectrometer response for each PAH relative to the internal standard is determined using check standards at concentrations of 250 ng/mL. Daily response factors for each compound are compared to the initial calibration curve. If the average daily response

factors for all analytes is within ±15% of the calibration value, analyses may proceed. If, for any analyte, the daily response factor exceeds ±35 percent of calibration value, a five-point calibration must be repeated for that compound prior to the analysis of samples.

Qualitative identification of target compounds is based on relative retention time (RRT) criteria. Table. 3 contains example RRT data for (unsubstituted) PAHs. RRT windows for alkyl homologues is based on analysis National Institute of Standards and Technology (NIST) SRM 1582 or other suitable reference oil.

5.0 DAILY GC/MS PERFORMANCE TESTS

The mass spectrometer is tuned to perfluorotributylamine (PFTBA) criteria established by the manufacturer.

6.0 GAS CHROMATOGRAPHY/MASS SPECTROMETRY ANALYSES

Just prior to analysis, an aliquot of internal standard solution is added to the sample producing a final internal standard concentration of approximately 40 ng/mL. Representative aliquots are injected into the capillary column of the gas chromatograph using the following conditions:

Injector Temp:	300°C
Transfer Line Temp:	280°C
Initial Oven Temp:	40°C
Initial Hold Time:	0 min.
Ramp Rate:	10°C
Final Temperature:	300°C
Final Time:	4 min.

The effluent from the GC capillary column is routed directly into the ion source of the mass spectrometer. The MS is operated in the selected ion monitoring (SIM) mode using appropriate windows to include the quantitation and confirmation masses for the PAHs listed in Table 4. For all compounds detected at a concentration above the MDL the confirmation ion is checked to confirm its presence.

Compounds identified and quantified below the MDL are reported. If the concentration of any target compound in a sample exceeds the linear range defined by the standards above, the extract is diluted and reinjected.

Table 3. Relative Retention Times and Confidence for the Compounds Associated with the Low-Level PAH Methodology[a].

	Absolute Retention Time (minutes)	Average RRT	SD	Percent RSD	95 Percent Confidence Limits
Naphthalene-d_8(Surr.)	6:46	1.010	0.017	2.289	0.899-0.767
Naphthalene	6:52	1.006	0.017	2.289	0.701-0.769
2-Methylnaphthalene	8:10	0.872	0.017	2.084	0.798-0.866
1-Methylnaphthalene	8:36	1.200	0.017	2.055	0.814-0.882
Acenaphthylene	10: 25	0.962	0. 018	1.822	0.927-0.988
Acenaphthene	10:72	0.988	0.018	1.849	0.952-1. 024
Fluorene-d_{10}(IS)	11:50	0.872	0.015	1.735	0.842-0.902
Fluorene	11:96	0.875	0.015	1.745	0.845-0.805
Dibenzothiophene	14:15	0.974	0.018	1.817	0.942-1.006
Phenanthrene	14:35	0.988	0.018	1.589	0.958-1.020
Anthracene	14:45	0.994	0.016	1.597	0.962-1.026
Fluoranthene	17:33	1.130	0.017	1.461	1.096-1.164
Pyrene	17:87	1.157	0.017	1.443	1.123-1.191
Benz[a]anthracene	20:96	0.873	0.012	1.325	0.849-0.897
$Chrysene_{12}$(Surr.)	20:99	0.897	0.012	1.320	0.850-0.898
Chrysene	21:04	0.876	0.012	1.320	0.852-0.900
Benzofluoranthenes	23:52	0.960	0.014	1.501	0.932-0.988
Benzol [e]pyrene	24:08	0.984	0.016	1.590	0.952-1.016
Benzol[a]pyrene	24:19	0.988	0.016	1.615	0.956-1.020
Perylene	24:38	0.996	0.016	1.844	0.964-1.028
Indeno [1,2, 3-cd] pyrene	26:99	1.114	0.025	2.276	1.064-1.164
Dibenz[a,h]anthracene	27:08	1.113	0.031	2.743	1.051-1.175
Benzo [g, h, i] perylene	27:71	1.149	0.028	2.422	1.093-1.205

(a) This table is to serve as an example. Absolute retention times may vary depending on the length and condition of the GC column.

7.0 CALCULATIONS

7.1 Qualitative Identification

The extracted ion current profiles of the primary m/z and the confirmatory ion for each analyte must meet the following criteria:

The characteristic masses of each parameter of interest must maximize in the same or within one scan of each other. The retention time must fall within ±30 s of the retention time of the authentic compound or alkyl homologue grouping determined by analysis of reference material.

Note: The alkylated PAH homologue groupings (e.g. C_3 naphthalene) appear as clusters of isomers. The pattern of each cluster and the retention time window for the cluster is established by analysis of reference crude oil. The cluster is integrated in its entirety and the total response used for quantification.

The relative peak heights of the primary ion compared to the confirmation or secondary ion masses must fall within ±30 percent of the relative intensities of these masses in a reference mass spectrum. The reference mass spectrum is obtained from reference material. In some instances, a compound that does not meet secondary ion confirmation criteria may still be determined to be present in a sample after close inspection of the data by the mass spectroscopist. Supportive data includes the presence of the secondary ion, but the ratio is greater than ±30 percent of the primary ion which may be caused by an interference of the secondary ion. The data not meeting these criteria is reported but appropriately qualified in the data base.

7.2 Quantitation

The following formula is used to calculate the response factors of the internal standard relative to each of the calibration standards.

$$RF = (A_S C_{IS}) / (A_{IS} C_S)$$

where:

A_S = Area of the characteristic ion for the parameter to be measured.
A_{IS} = Area of the characteristic ion for the internal standard.
C_{IS} = Concentration of the internal standard (ng/mL).
C_S = Concentration of the parameter to be measured (ng/mL).

Table 4. Parameters for Target Analytes.

Analyte	Quant. Ion	Conf. Ions	% Rel. Abund. of Conf. Ions
d_8-Naphthalene	136	134	15
Naphthalene	128	127	15
C_1-Naphthalenes (including isomers)	142	141	80
C_2-Naphthalenes	156	141	ND
C_3-Naphthalenes	170	155	ND
C_4-Naphthalenes	184	169,141	ND
d_{10}-Acenaphthene	164	162	95
Acenaphthylene	152	153	15
Biphenyl	154	152	30
Acenaphthene	154	153	98
d_{10}-Fluorene	176	174	85
Fluorene	166	165	95
C_1 Fluorenes	180	165	100
C_2-Fluorenes	194	179	25
C_3-Fluorenes	208	193	ND
d_{10}-Phenanthrene	188	184	ND
Phenanthrene	178	176	20
Anthracene	178	176	20
C_1-Phenanthrenes/anthracenes	192	191	60
C_2-Phenanthrenes/anthracenes	206	191	ND
C_3-Phenanthrenes/anthracenes	220	205	ND
C_4-Phenanthrenes/anthracenes	234	219,191	ND
Dibenzothiophene	184	152,139	15
C_1-Dibenzothiophenes	198	184,197	25
C_2-Dibenzothiophenes	212	197	ND
C_3-Dibenzothiophenes	226	211	ND
Fluoranthene	202	101	15
d_{12}-Chrysene	240	236	ND
Pyrene	202	101	15
C_1-Fluoranthenes/pyrenes	216	215	60
Benzo [a] anthracene	228	226	20
Chrysene	228	226	30
C_1-Chrysenes	242	241	ND
C_2-Chrysenes	256	241	ND
C_3-Chrysenes	270	255	ND
C_4-Chrysenes	284	269,241	ND
d_{12}-Benz (a)pyrene	264	260	20
Benzo [b] fluoranthene	252	253,125	30, 10
Benzo [k] fluoranthene	252	253, 125	30, 10
Benzo (e) pyrene	252	253	30,10
Perylene	264	253	20
d_{12}-Perylene	264	260	ND
Benzo [a] pyrene	252	253, 125	30, 10
Indeno[1,2,3-c,d]pyrene	276	277, 138	25,30
Dibenzo [a,h] anthracene	278	279, 139	25,20
Benzo [g,h,i]perylene	276	277, 138	25,20

ND = Not determined

Note: Response factor of alkyl homologues is assumed to be equal to that of respective unsubstituted compounds. Based on these response factors, sample extract concentrations for each PAH and alkyl homologue grouping is calculated using the following formula:

$$Ce = \frac{(A_s)(I_s)}{(A_{Is})(RF)}$$

where:

Ce = Sample extract concentration (ng/mL).
A_S = Area of the characteristic ion for the parameter to be measured.
A_{is} = Area of the characteristic ion for the internal standard.
I_S = Amount of internal standard added to each extract (ng/mL).

The actual sample concentration (C) for each compound is calculated by the following formula:

$$C = (Ce) \times \frac{V_e}{V_s}$$

where:

C = Concentration in sample (ng/L).
V_E = The final extract volume (mL).
V_S = The original volume of sample extracted (L).

Alkyl homologues are reported as total C-1, total C-2, etc. Specific isomers are also reported as detailed in Table 1.

Analyte concentrations can be corrected based on the recoveries of surrogates if requested.

8.0 QUALITY CONTROL/QUALITY ASSURANCE (QA/QC) REQUIREMENTS

8.1 GC/MS Tuning

The GC/MS is tuned as described in Section 5.0.

8.2 GC/MS Initial Calibration and Continuing Calibration Checks

A five-point response factor calibration curve is established demonstrating the linear range of the analysis.

After every 8-10 sample analyses, the mass spectrometer response factor (RF) for each PAH of interest (Table 1) relative to the internal standard is determined.

These daily response factors for each compound are compared to the initial calibration curve. The percent difference is calculated using the following equation:

$$\text{Percent Difference} = \frac{\text{RFI - RFC x 100}}{\text{RFI}}$$

where:

RFI = Average response factor from initial calibration.

RFC = Response factor from current verification check standard.

If the average daily response factors are within ±15 percent of the calibration value, the analysis may proceed. If, for any individual analyte, the daily response factor is not within ±25 percent of the corresponding calibration curve value, a five-point calibration curve must be repeated for that compound prior to the analysis of samples.

8.3 Method Blank Analysis

An acceptable method blank analysis may not contain the analytes of interest at concentrations 3 times greater than MDL. If the method blank exceeds these criteria, the analytical procedure is out of control and the source of the contamination must be investigated and corrective measures taken and documented before further sample analysis proceeds.

8.4 Surrogate Compound Analysis

The laboratory will spike all samples and quality control samples with deuterated PAH surrogate compounds (SUR). The surrogate compounds are spiked into the sample prior to extraction and measure sample matrix effects associated with sample preparation and analysis. They will include

naphthalene-d_8, acenaphthene-d_{10}, phenanthrene-d_{10}, chrysene-d_{12} and perylene-d_{12}. The recovery of this surrogate is monitored in each sample using the response of the I.S. that is added to the final extract.

$$\text{Percent SUR recovery} = (A_{SUR} \times C_{IS})/(C_{SUR} \times A_{IS} \times RF_{SUR})\ 100$$

where:

A_{IS} = Area of the characteristic ion for the appropriate internal standard
A_{SUR} = Area of the characteristic ion for the surrogate
C_{SUR} = ng of deuterated surrogate added to the sample
C_{IS} = ng of deuterated internal standard added to the sample extract
RF_{SUR} = Response factor for the surrogate.

Analyte concentrations can be reported as corrected or uncorrected for surrogate recoveries.

The laboratory will take corrective action whenever the recovery for any surrogates is less than 20% or greater than 130%.

The following corrective action will be taken:

a. The calculations are checked to assure there are no errors.

b. The internal standard and surrogate solutions are checked for degradation, contamination, etc., and the instrument performance is checked.

c. If the surrogate recovery is outside the control limits, the secondary ion may be used to check the quantitation of the surrogate. If the secondary ion is within the control limits, this recovery is appropriately annotated.

d. If the upper control limit is exceeded for a surrogate, and the instrument calibration and surrogate standard concentration are in control, it is concluded that an interference specific to the surrogate was present that resulted in high recovery and that this interference does not affect the quantitation of other target compounds. The presence of this type of interference is confirmed by evaluation of chromatographic peak shapes.

e. If the surrogate cannot be measured because the sample required dilution or only a portion of the sample is analyzed, no corrective action is required. The surrogate recovery is appropriately qualified.

f. The sample or extract is reanalyzed if the steps above fall to reveal a problem. If reanalysis of the extract yields surrogate recoveries within the stated limits, then the reanalysis data is reported. If reanalyses does not yield acceptable recoveries, the data will be listed as out of control.

8.5 Matrix Spike Analysis

The laboratory spikes and analyzes a matrix spike and matrix spike duplicate (MS/MSD) with every 20 samples or with every sample set, whichever is more frequent. A sample is randomly chosen, split into three subsamples and two subsamples are fortified with the matrix spike. The compounds are listed in Table 2. The acceptable matrix spike recovery criteria for water, sediment and tissue analysis are:

- The average recoveries for all 25 compounds must fall between 40 and 120 percent.

If the matrix spike criteria are not met, the matrix spike analysis will be repeated. If the subsequent matrix spike analysis meets the criteria, then the reanalysis data is reported.

8.6 Reference Material

When available, a standard reference material is analyzed with each batch of samples. Laboratory control charts are established for the PAH levels in the SRM. The average percent difference for the target compounds should not exceed 20% of the mean of all previous values, and no single compound/isomer grouping should deviate by more than 35% mean value of all previous determinations

8.7 Method Detection Limit

The actual analytical method detection limit (MDL) are determined following procedures outlined in Federal Register (1984), Vol. 49, No. 209: 198-199.

9.0 REPORTING

9.1 Reporting Units

All data are reported in units of ng/g dry weight for sediment and ng/g dry weight for tissue samples.

9.2 Minimum Method Performance Criteria

The minimum method performance standard for sediments are 5 ng/g for individual PAH compounds. The minimum method performance standard for biological tissue is 20 ng/g for individual PAH compounds.

9.3 Significant Figures

Results are reported to three (3) significant figures.

9.4 Surrogate Recoveries

Surrogate recoveries are reported for each sample analyzed.

9.5 Matrix Spike

Matrix spike recoveries are reported for each batch of samples.

Note: The effective minimum performance standard can be adjusted by decreasing final sample volume, increasing sample amount and/or increasing volume injected on the GC-FID or GC/MS.

10.0 EXAMPLE FORMS AND CHROMATOGRAMS

10.1 Analysis Request Form

10.2 Typical mass fragmentograms from GC/MS analysis of matrix spike given in Table 2.

NOAA - S & T ANALYSIS REQUEST FORM

Requestor: _____ Return To: _____ Date: _____ Page #: _____

Extraction Date: _____

☐ FID Date Analyzed: _____ Method: _____ 5-pt Cal: _____

☐ SIM Date Analyzed: _____ Method: _____ 5-pt Cal: _____

SURROGATE ADDED		*INTERNAL STD ADDED*	
Descriptor	Amount	Descriptor	Amount

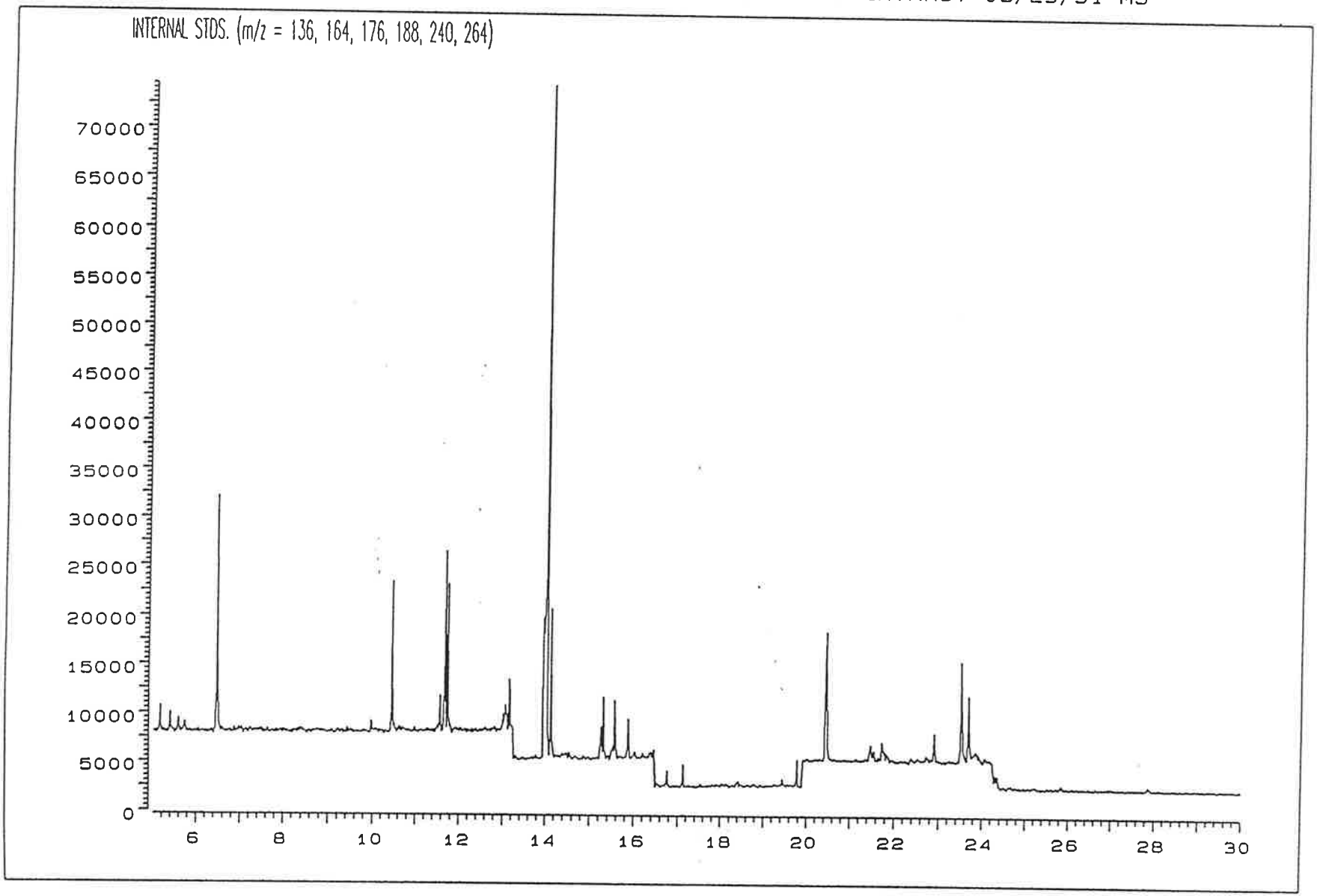
Run Sequence:

	File #	Sample Description	Sample Wt/Vol.	Dil. Factor
1		Solvent Blank		
2				
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				
13				
14				
15				
16				
17				
18				
19				
20				
21				
22				
23				
24				
25				

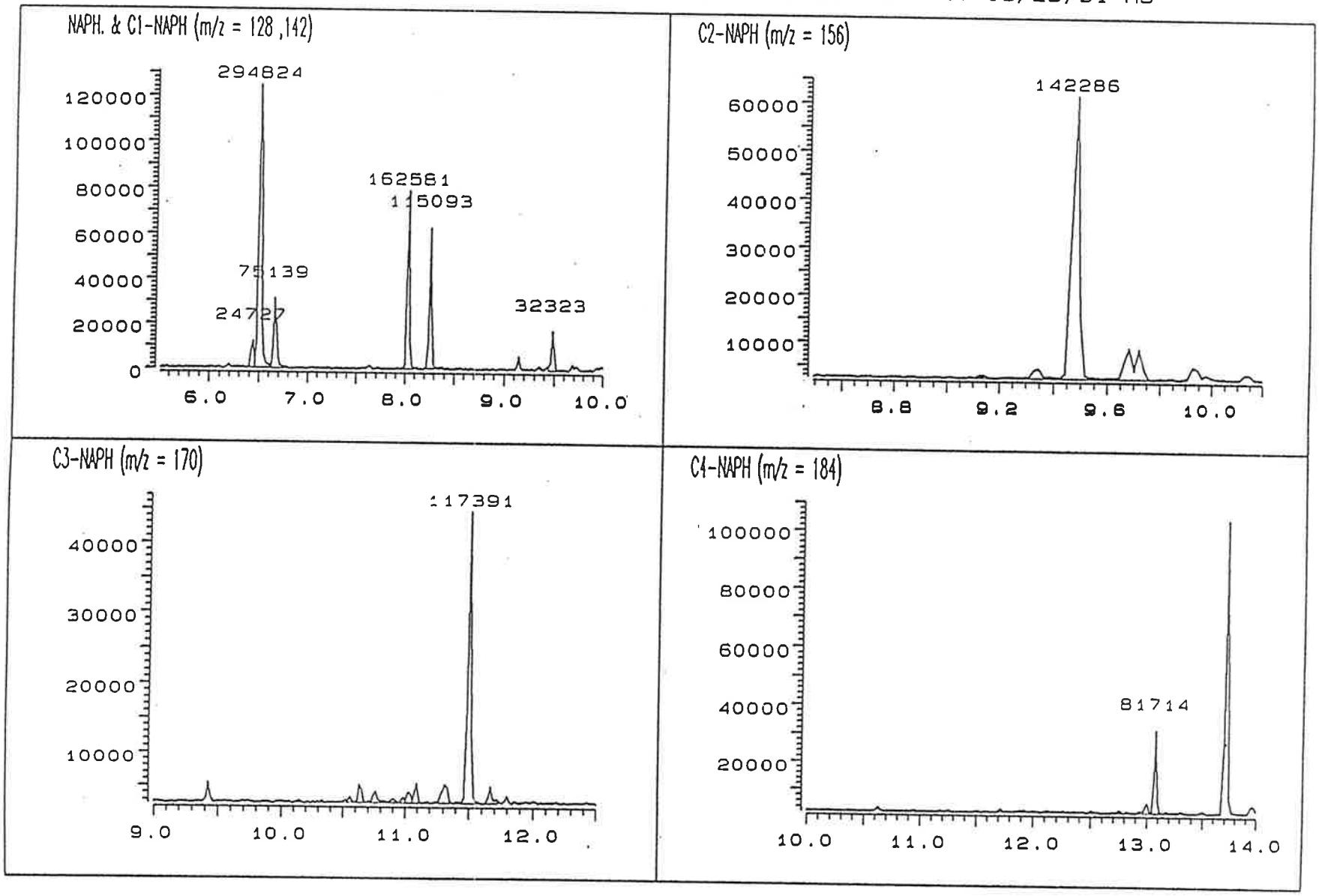
	Descriptor	Amount	Smpl Position
MATRIX SPIKE			
SRM			
BLANK			

A copy of this form to accompany sample set at ALL TIMES

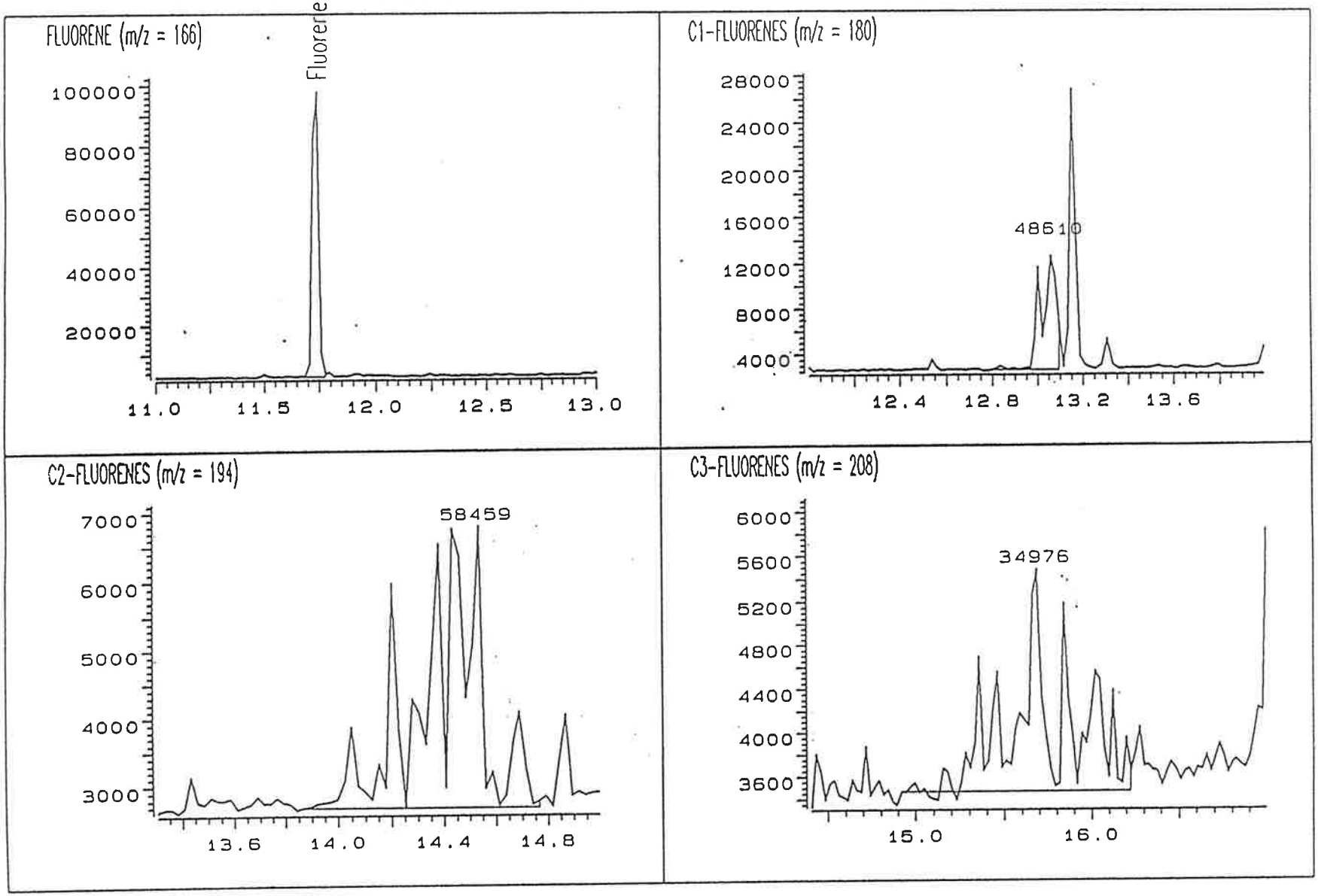
FILE: >Q0878 NOAA SPK (N0515) NP351 2ul/1000ul EXTRACT 03/29/91 M5



FILE: >Q0878 NOAA SPK (N0515) NP351 2ul/1000ul EXTRACT 03/29/91 M5



FILE: >Q0878 NOAA SPK (N0515) NP351 2ul/1000ul EXTRACT 03/29/91 M5



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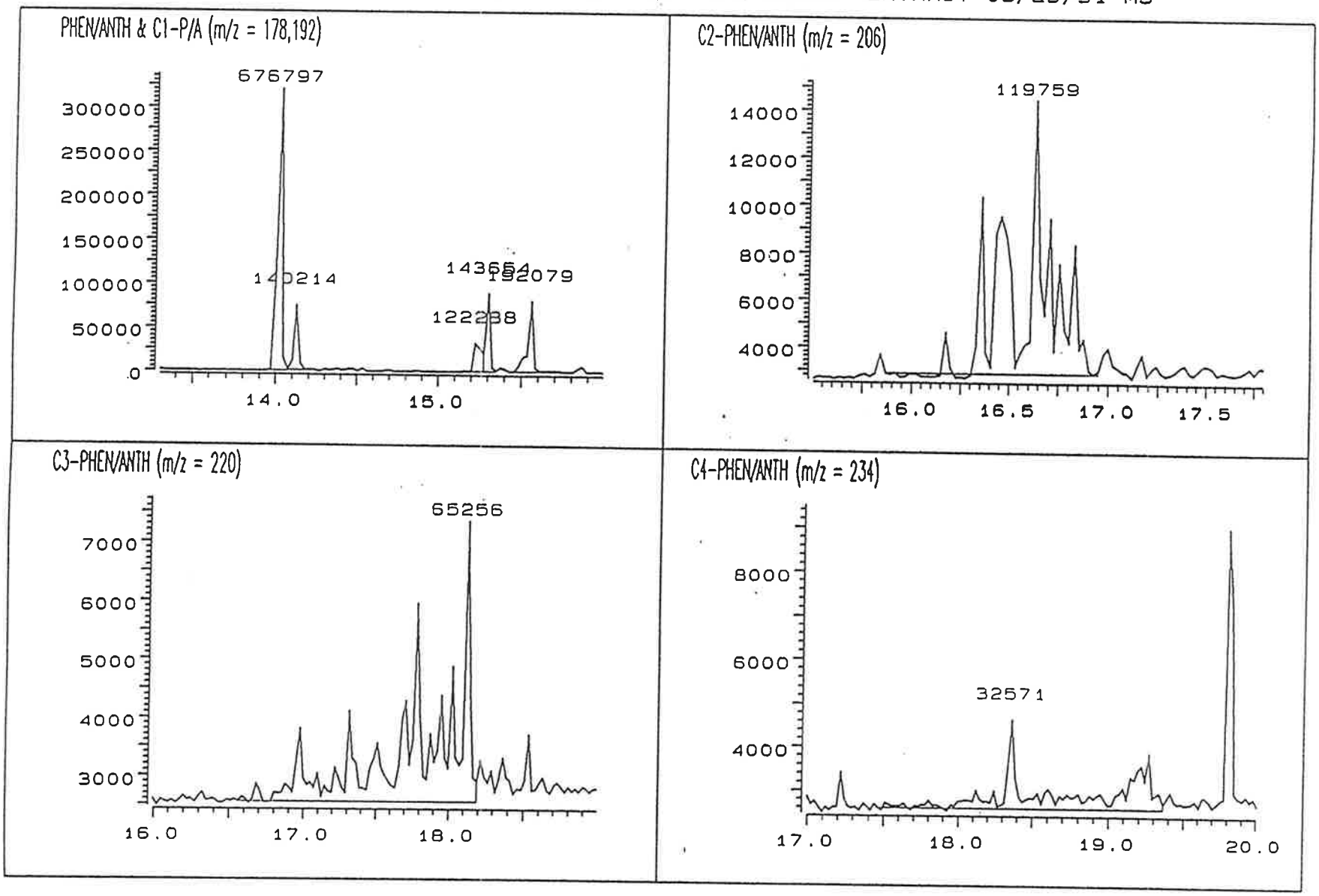

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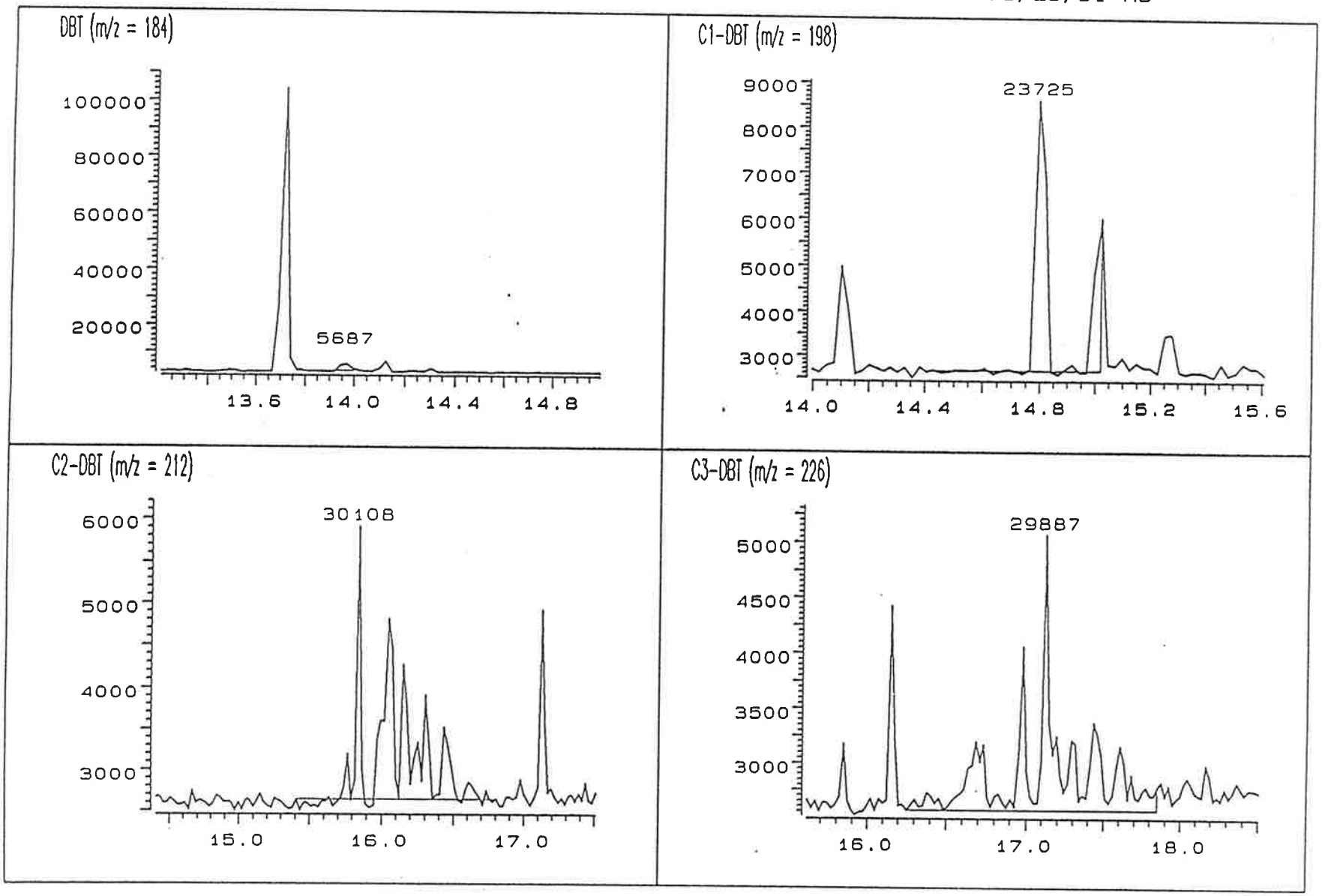

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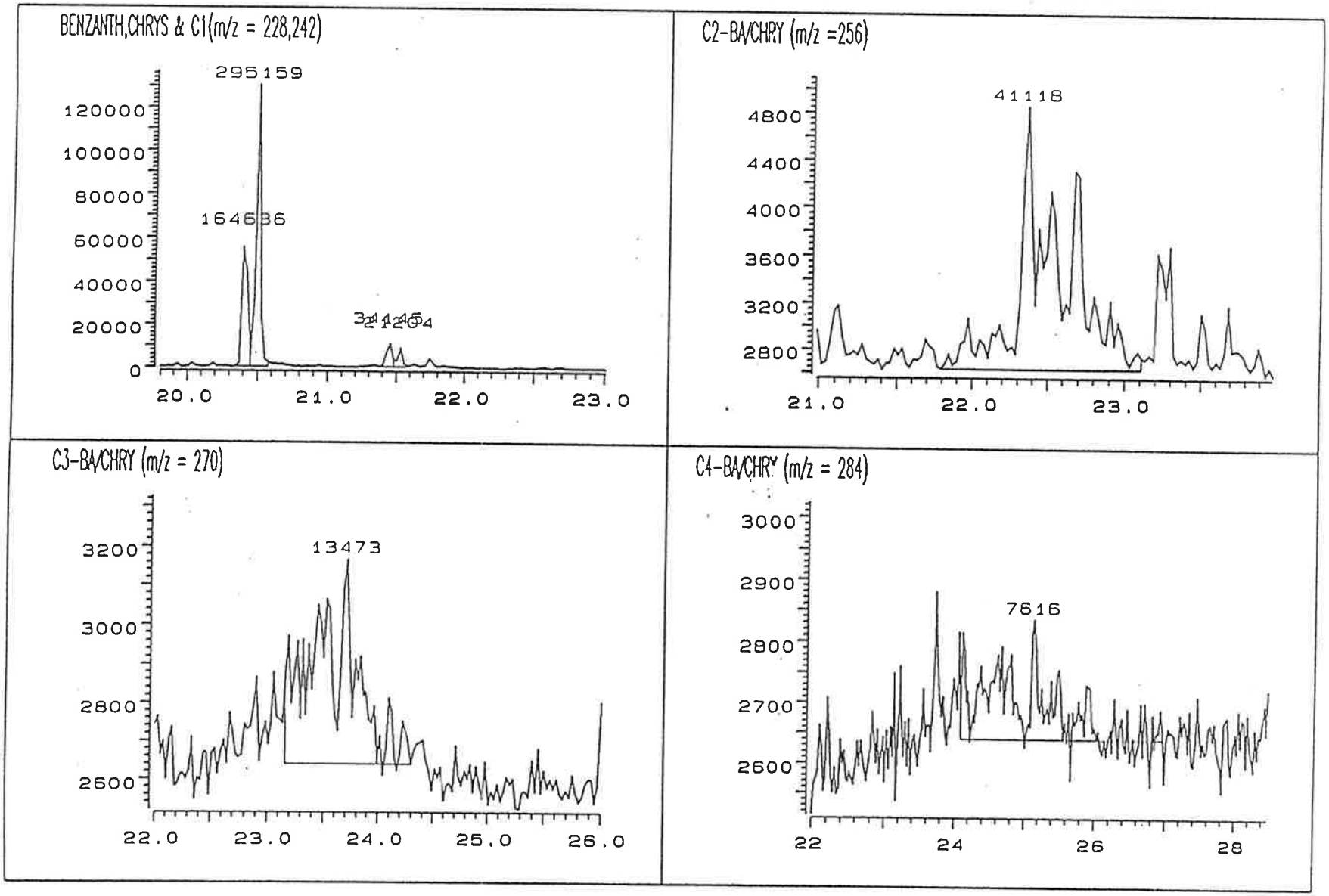
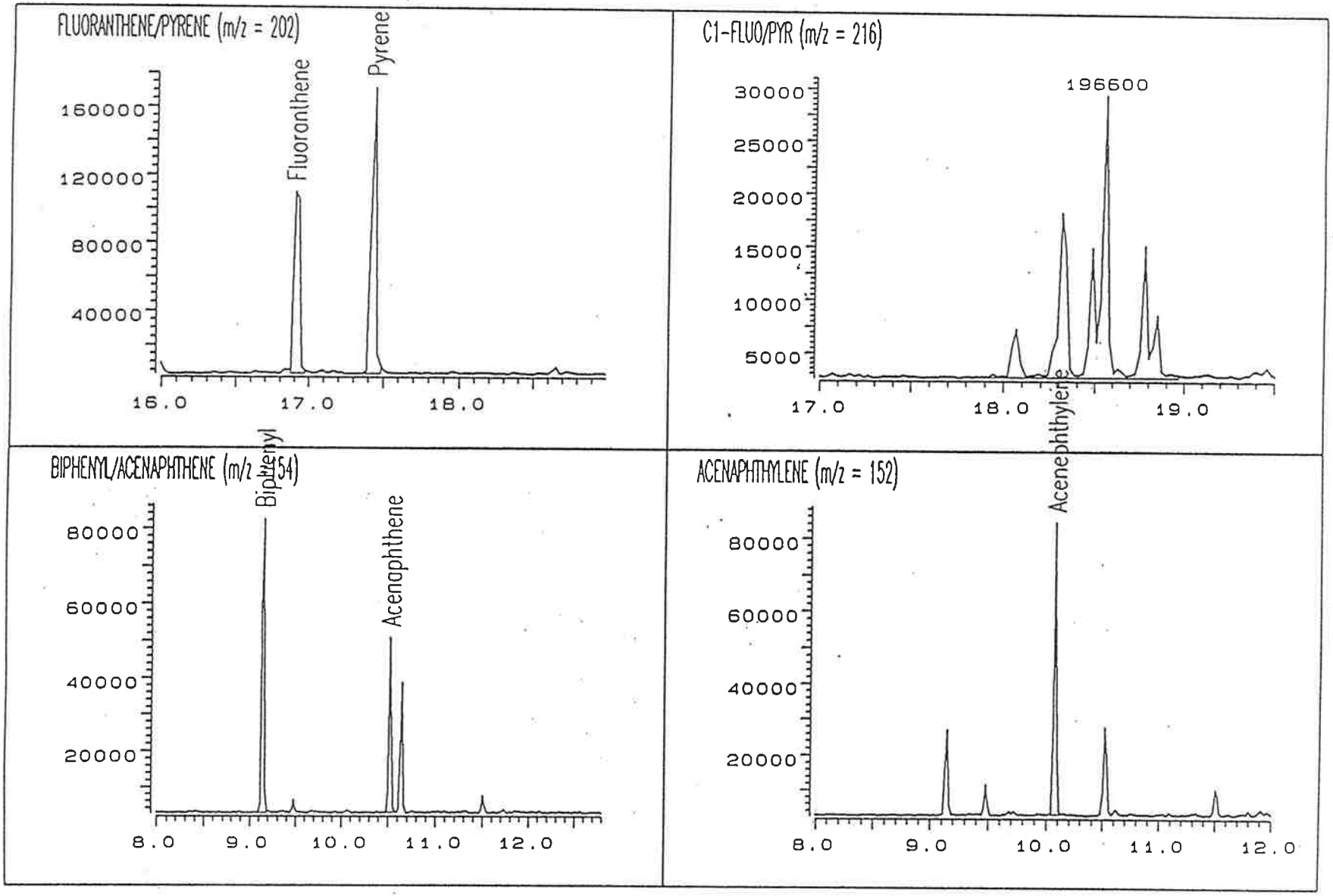
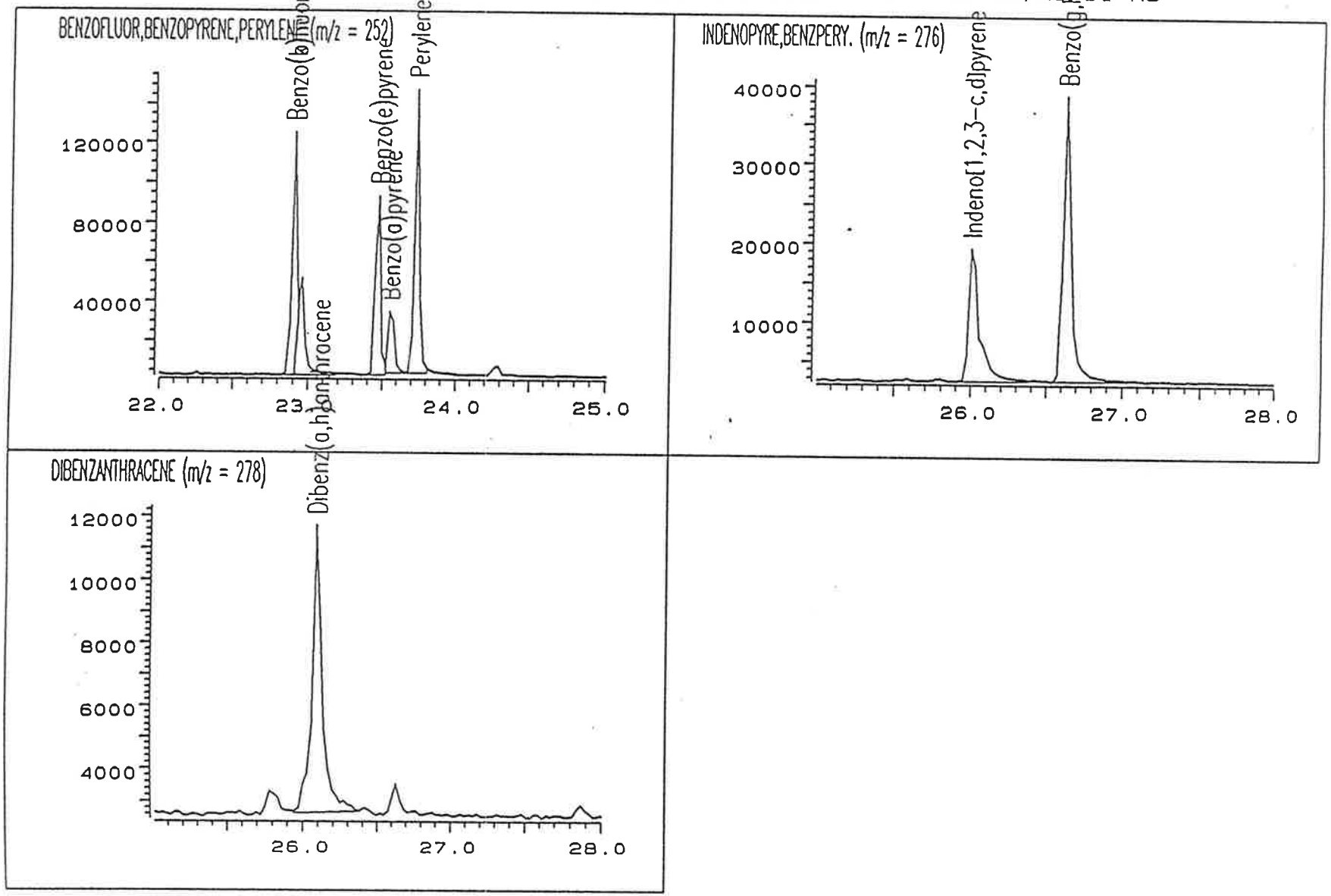


FILE: >Q0878 NOAA SPK (N0515) NP351 2ul/1000ul EXTRACT 03/29/91 M5



FILE: >QQ078 NOAA SPK (N0515) NP351 2ul/1000ul EXTRACT 03/29/91 M5



QUANTITATIVE DETERMINATION OF CHLORINATED HYDROCARBONS

1.0 INTRODUCTION

The quantitative method described in this document determines chlorinated hydrocarbons (e.g. chlorinated pesticides and PCBs) in extracts of biological tissues and sediments. The method is based on high resolution, capillary gas chromatography using electron capture detection (GC/ECD).

Extracts should be prepared as described in GERG SOP's-ST01 and ST02 for biological tissues and sediments, respectively.

Sample collection, preservation, storage and holding times are discussed under the analytical procedures for sample extraction and purification.

2.0 APPARATUS AND MATERIALS

A gas chromatograph with a split/splitless injection system, capillary column capability and a electron capture detector (ECD) is utilized.

2.1 GC Column

A 30-m long x 0.25-mm I.D. fused silica capillary column with DB-5 bonded phase (J&W Scientific or equivalent) should be used. The column should provide good resolution of chlorinated hydrocarbons, surrogates and internal standards.

2.2 Autosampler

The autosampler is capable of making 1-4 µL injections.

3.0 REAGENTS

3.1 Calibration Solution

The calibration solution is comprised of, at a minimum, the chlorinated hydrocarbons listed in Table 1.

Table 1. Chlorinated Hydrocarbons of Interest.

Chlorinated Pesticides

Aldrin	Heptachlor Epoxide	o-p' DDT
alpha-Chlordane	Hexachlorobenzene	p-p' DDT
Dieldrin	Lindane	o-p' DDD
Endrin	Mirex	p-p' DDD
Heptachlor	Trans-Nonachlor	o-p' DDE
		p-p' DDE

Polychlorinated Biphenyls

Dichlorobiphenyls	Pentachlorobiphenyls	Heptachlorobiphenyls
7*	100	178
8	88	187/182
15	92	183
	84	185
Trichlorobiphenyls	101	174
18	99	177
24	83	171
16/32	97	172
26	87	180
25	85	191
31	110	170
28	82	189
33	107/108	
22	118	Octachorobiphenyls
37	114	202
	105	200
Tetrachlorobiphenyls	126	201
45		196
46	Hexachorobiphenyls	195
52	136	194
49	151	205
47/48	144	
44	149	Nonachlorobiphenyls
42	146	208
41/64	153	206
40	141	
74	137	Decachlorobiphenyls
70	138	209
66	158	
60/56	129	
77	159	
	128	
	167	

*PCB number from: Ballschmiter, K. and M. Zell, 1980, Analysis of Polychlorinated Biphenyls (PCB) by Glass Capillary Gas Chromatography. *Freesenius Z. Anal. Chem.*, 302: 20-31.

Calibration standards should be prepared in the concentration range of 5 to 200 ng/ml (at four concentrations) at a minimum. Internal standard and surrogate compounds should be added at 100 ng/ml to all calibration standards.

3.2 Surrogate Spiking Solution

The surrogate compounds for all sample types are DBOFB, εHCH, PCB-103, and PCB-198. A surrogate solution is made by weighing an appropriate aliquot of pure material into a volumetric flask and diluting to volume with hexane. Surrogate standards are added to each sample at a concentration of ~10 times the MDL. For higher concentrations of chlorinated hydrocarbons the surrogate standard concentrations are appropriately increased.

3.3 Internal Standard Solution

The internal standard for this analysis is TCMX. An internal standard solution is made by weighing an appropriate aliquot of pure material into a volumetric flask and diluting to volume with hexane. Internal standard should be added to each sample extract to obtain a final concentration of approximately 100 ng/ml. For higher concentrations the internal standard concentration is appropriately increased.

3.4 Matrix Recovery Spiking Solution

The matrix spiking solution consists of chlorinated pesticides and PCBs listed on Table 1.

The matrix spike is added to samples at a concentration ~10x the MDL. If higher concentrations are expected the matrix spike is appropriately increased.

3.5 Retention Index Solution

The calibration mixture is also used as a retention index solution.

4.0 PROCEDURE

4.1 Sample Extraction and Purification

Tissue samples are extracted and purified following GERG SOP-ST01. Sediment samples are extracted and purified following GERG SOP-ST02.

4.2 High Resolution GC-ECD Analysis

4.2.1 GC Conditions

For the analysis of chlorinated hydrocarbons, the analytical system, or its equivalent, should include at a minimum:

Instrument:	Hewlett-Packard 5880A or Varian 3500 Series
Features:	Split/splitless capillary inlet system, HP-1000 LAS 3357 data acquisition system
Inlet:	Splitless
Detector:	Electron Capture
Column:	0.25-mm I.D. x 30-m DB-5 fused silica capillary column (J&W Scientific) or equivalent
Gases:	
Carrier:	Helium 1 ml/min
Make-Up:	Argon/methane (95/5) or Nitrogen, 20 ml/min.
Confirmation Column:	0.20 mm ID x 25-m HP-17 fused silica capillary column (Hewlett Packard) or equivalent
Temperatures:	
Injection port:	275°C
Detector:	325°C
Oven Program:	100°C for 1 min., then 5°C/min. to 140°C, hold 1 min.; 1.5°C/min to 250°C, hold 1 min.; 10°C/min to 300°C, hold 5 min.

The GC oven temperature program may be modified to improve resolution.

Calibration: 40, 80, and 200 ng/ml)	Five-point calibration (5 or 20,
Quantification:	Internal standard/calibration

4.2.2 Calibration

The GC calibration is performed at a minimum of four concentrations. One of the concentration levels is near, but above the MDL. The remaining concentrations correspond to the expected range of the sample analytes. A concentration range of 5 to 200 ng/ml is recommended. An average calibration factor from the authentic standard of each individual compound is used to calculate sample analyte concentrations. The initial calibration is verified by the measurement of calibration standards after every 6 samples.

A mid-level standard is analyzed immediately prior to conducting any analyses, and after each group of 6 samples. The response factor criteria for an in control calibration check is ±15% on average from the initial calibration and no single analyte should exceed ±25%.

4.2.3 Sample Analysis

Chlorinated hydrocarbon analyses are initiated with a calibration check, followed by 6-8 samples, and ending with a calibration check. If the response factor for any analyte in the calibration check fails to meet the criteria established in Section 4.2.2, the instrument is recalibrated. All samples that were injected after the standard exceeded the criteria must be reinjected or recalculated based on the analysts review of the data.

Sample injections of 1 to 4 µL are made with an autosampling device.

If the response for any peak exceeds the highest calibration solution, the extract is diluted and reanalyzed.

4.2.4 Calculations

Concentrations in samples are based on surrogate standards added. All analyte concentrations are calculated from specific surrogates. The internal standard is used to calculate surrogate recoveries.

5.0 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) REQUIREMENTS

5.1 Initial Calibration and Continuing Calibration Checks

Prior to the analyses, a five-point calibration curve establishes the response of the detector. The calibration curve is prepared using a non-linear calibration equation of the form:

$$Y = A(x)^B$$

$$Y = (C_a/C_{su}) = A * (A_a/A_{su})^B$$

where:

A = Constant, slope of the line fit
B = Constant, polynomial coefficient for the line fit
C_a = Concentration of the analyte to be measured (ng/ml).
C_{su} = Concentration of the surrogate standard (ng/ml) (PCB 103).
A_a = Area for the analyte to be measured.
A_{su} = Area for the surrogate standard (PCB 103).

For every 6 sample analyses or at least once daily, the calibration for each compound of interest is determined relative to the surrogate standard and compared to the initial calibration curve. If the average concentration for all analytes is within ±15 percent of the corresponding value, the analysis may proceed. If, for any individual analyte, the daily response factor calculated concentration exceeds ±25 percent of the corresponding value, a five-point calibration curve must be repeated for all compounds prior to the analysis of the samples. All samples are calculated from the initial calibration.

5.2 Method Blank Analysis

An acceptable method blank analysis does not contain any target compound at concentration 3 times greater than the MDL. If the method blank does not meet these criteria, the analytical system is out of control and the source of the contamination must be investigated, corrective measures taken, and documented before further sample analysis proceeds.

5.3 Surrogate Standards Analysis

All samples and quality control samples are spiked with DBOFB, PCB 103 and PCB 198. The surrogate standard solution will be spiked into the sample prior to extraction to measure individual sample matrix effects associated with sample preparation and analysis.

The laboratory will take corrective action whenever the recovery of DBOFB, PCB 103 and PCB 198 is outside of 40 to 130 percent for sediment and tissue matrices.

The following corrective action will be taken when an out of control event occurs:

a. Calculations are checked to assure that no errors have been made.

b. The surrogate standard solutions are checked for degradation, contamination, etc., and instrument performance is checked.

c. If the surrogate could not be measured because the sample required dilution or only a portion of the sample was analyzed, or matrix interference occurs with only one surrogate, no corrective action is required. The surrogate recovery is properly annotated.

d. If the steps above fail to reveal a problem, the sample or extract is reanalyzed. If reanalysis of the extract yields surrogate recoveries within the stated limits, then the reanalysis data is reported. If upon reinjection QA criteria are still violated, the sample will be submitted for re-extraction if sufficient sample is available. If the sample was completely consumed, the data will be reported but designated as outside the QA criteria.

5.4 Matrix Spike Analysis

The laboratory spikes and analyzes a matrix spike and a matrix spike duplicate (MS/MSD) every 20 samples or with every sample set, which ever is more frequent. A sample is randomly chosen, split into three subsamples and two subsamples are fortified with the matrix spike. The acceptable matrix spike recovery criteria for water, sediment and tissue analysis are:

- The average recoveries for all compounds must fall between 40 and 120 percent.

If the matrix spike criteria are not met, the matrix spike will be reinjected on the GC. If the reinjected matrix spike analysis meets the criteria, then the reanalysis data is reported. If not, the entire batch of samples are submitted for re-extraction if sufficient sample is available. If the sample was completely consumed the data will be reported but designated as outside the QA criteria.

5.5 Method Detection Limit

The method detection limit is determined following the procedures outlined in Federal Register (1984), Vol. 49, No. 209: 198- 199.

5.6 GC Resolution

The target compounds, surrogates and internal standard must be resolution from one another and from interfering compounds.

5.7 Reference Sample Analysis

When available, reference materials will be analyzed for chlorinated hydrocarbons. One sample will be analyzed per batch of samples, and the results will be used to establish laboratory QC charts. The result should agree within ±25% of the mean of the previously reported data. The data produced are used to construct control charts.

6.0 CALCULATIONS

6.1 Chlorinated Hydrocarbon Calculations

All calculations are based on the surrogates added before extraction and purification. The actual sample concentration (C, see section 7.1 for reporting units) for each compound is calculated by the following formula:

$$C = A * (A_a/A_{su})^{B} * (I_{su}/S_w)$$

where:

A = Constant, slope of line fit
B = Constant, polynomial coefficient for the line fit
A_a = Area for the analyte to be measured.
A_{su} = Area for the surrogate standard (PCB 103).

I_{su} = Amount of surrogate standard added to the sample.
S_w = Sample weight.

6.2 Calculation Notes

6.2.1 To each sample, a specific amount of surrogate standard is added. The recovery of these compounds is monitored in each sample using the response of TCMX the internal standard (I_{gi})s added to the final extract.

$$\text{Percent recovery} = (R_1 * R_2 / R_3) * (I_{su} / I_{gi}) * 100$$

where:

R_1 = (Analyte peak area / surrogate peak area) in sample.
R_2 = (Analyte concentration / surrogate concentration) in reference.
R_3 = (Analyte peak area / surrogate peak area) in reference.
I_{gi} = Amount of internal standard added to sample just prior to GC analysis.
I_{su} = Amount of surrogate standard added to sample.

7.0 REPORTING

7.1 Reporting Units

Data is reported in ng/g dry weight for biological tissues and sediments.

7.2 Minimum Method Performance Criteria

The minimum method performance standard for tissues and sediments is 2 ng/g for individual compounds.

7.3 Significant Figures

Results are reported to three (3) significant figures.

7.4 Surrogate Recovery

Surrogate recoveries are reported for each sample analyzed.

7.5 Matrix Spike

Matrix spike recoveries are reported for each batch of samples analyzed.

7.6 Reference Materials

When available the results of the analysis of reference materials is reported for each batch of samples analyzed.

Note: The effective minimum performance standard can be adjusted by decreasing final sample volume, increasing sample amount and/or increasing volume injected on the GC-ECD.

7.7 If confirmation is required on a second capillary column of different polarity an HP-17 of equivalent is used. GC operating conditions are those detailed in Section 4.2.1.

QUANTITATIVE DETERMINATION OF ALIPHATIC HYDROCARBONS AND UCM (UNRESOLVED COMPLEX MIXTURE)

1.0 INTRODUCTION

The quantitative method described in this document determines aliphatic hydrocarbons in extracts of water, sediments and tissues. A modified EPA Method 8100 for the instrumental analysis of environmental samples for normal alkanes, pristane and phytane, and the unresolved complex mixture is detailed. The method is based on high resolution, capillary gas chromatography using flame ionization detection (GC/FID). This method quantitatively determines compounds from approximately n-C_{10} to n-C_{34}.

Extracts should be prepared as described in GERG SOP's-8901, 8902 and 8903 for water, sediment and biological tissues, respectively.

Sample collection, preservation, storage and holding times are discussed under the analytical procedures for sample extraction and purification.

2.0 APPARATUS AND MATERIALS

A gas chromatograph with a split/splitless injection system, capillary column capability and a flame ionization detector (FID) is utilized. The output from the detector is collected and processed by an automated HP-LAS 3357 data acquisition software package.

2.1 GC Column

A 30-m long x 0.32-mm I.D. fused silica capillary column with DB-5 bonded phase (J&W Scientific or equivalent) should be used. The column should provide baseline resolution of alkanes from n-C_{10} to n-C_{34}, phytane/n-C_{18}, pristane/n-C_{17}, surrogates and internal standards.

2.2 Autosampler

The autosampler is capable of making 1-4 µL injections.

3.0 REAGENTS

3.1 Calibration Solution

The calibration solution is comprised of, at a minimum, the n-alkanes and isoprenoids (commercially available) listed in Table 1.

Calibration standards should be prepared in the concentration range of 1.25 to 50 µg/mL (at five concentrations) at a minimum. Internal standard and surrogate compounds should be added at 2 µg/mL to all calibration standards.

3.2 Surrogate Spiking Solution

The surrogate compounds for all sample types are deuterated n-alkanes with 12, 20, 24 and 30 carbons. A surrogate solution is made by weighing an appropriate aliquot of pure material into a volumetric flask and diluting to volume with methylene chloride. Surrogates are added to each sample at a concentration of ~10x the MDL (i.e., 10 µl of 2 µg/mL to a final volume of 1 mL). For higher concentrations of oil the surrogate concentration is appropriately increased.

3.3 Internal Standard Solution

The internal standard for this analysis is deuterated n-C_{16}. An internal standard solution is made by weighing an appropriate aliquot of pure material into a volumetric flask and diluting to volume with methylene chloride. Internal standard should be added to each sample extract to obtain a final concentration of approximately 2 µg/mL. For higher concentrations of oil the internal standard concentration is appropriately increased.

3.4 Matrix Recovery Spiking Solution

The matrix spiking solution consists of alkanes from n-C_{10} to n-C_{34} and pristane (Table 1).

The matrix spike is added to samples at a concentration ~10x the MDL. For higher concentrations of oil the matrix spike is appropriately increased.

Table 1. Aliphatic Hydrocarbons (AH) of Interest

Compounds of Interest
N-C_{11}
N-C_{12}
N-C_{13}
N-C_{14}
N-C_{15}
N-C_{16}
N-C_{17}
Pristane
N-C_{18}
Phytane
N-C_{19}
N-C_{20}
N-C_{21}
N-C_{22}
N-C_{23}
N-C_{24}
N-C_{25}
N-C_{26}
N-C_{27}
N-C_{28}
N-C_{29}
N-C_{30}
N-C_{32}
N-C_{34}

3.5 Retention Index Solution

The calibration mixture is also used as a retention index solution.

4.0 PROCEDURE

4.1 Sample Extraction and Purification

Water samples are extracted and purified (optional) following GERG SOP-8901. Sediment samples are extracted and purified following GERG SOP-8902. Tissue samples are extracted and purified following GERG SOP-8903.

4.2 High Resolution GC-FID Analysis

4.2.1 GC Conditions

For the analysis of AH, the analytical system, or its equivalent, should include at a minimum:

Instrument:	Hewlett-Packard 5880A or HP 5890 Gas Chromatograph
Features:	Split/splitless capillary inlet system, HP-1000 LAS 3357 data acquisition system
Inlet:	Splitless
Detector:	Flame ionization
Column:	0.32-mm I.D. x 30-m DB-5 fused silica capillary column (J&W Scientific)
Gases:	
Carrier:	Helium 2 mL/min.
Make-Up:	Helium 33 mL/min.
Detector:	Air 360 mL/min.
	Hydrogen 33 mL/min.

Temperatures:

Injection port:	300°C
Detector:	300°C
Oven Program:	60°C for 1 min. then 6°C/min. to 300°C, hold 5 min.

The GC oven temperature program may be modified to improve resolution.

Daily Calibration:	Mid-level calibration solution; Retention index solution (20 µg/mL)
Quantification:	Internal standard/calibration

Note: The GC must be capable of the baseline resolution of all target compounds (n-alkanes, pristane, phytane), surrogates, and internal standards from each other and from interfering compounds.

4.2.2 Calibration

The GC calibration is performed at a minimum of five concentrations. One of the concentration levels is near, but above the MDL. The remaining concentrations correspond to the expected range of the sample analytes. A concentration range of 1.25 to 50 µg/mL is recommended. The detector is linear within this range. An average calibration factor from the authentic standard of each individual compound is used to calculate sample analyte concentrations. The initial calibration is verified by the measurement of calibration standards after every 8-10 samples. When possible, the RF for each individual saturated hydrocarbon is calculated from authentic material. If an individual saturated hydrocarbon is not in the calibration solution, a response factor (RF) is estimated from the average response factor of hydrocarbons eluting immediately before and after the compound.

The average response factor of all n-alkanes in the calibration standard is used for the UCM concentration calculations.

A mid-level standard is analyzed immediately prior to conducting any analyses, and after each group of 8-10 samples. The response factor criteria for an in control calibration check is ±15% on average from the initial calibration and no single analyte should exceed ±25%.

4.2.3 Retention Time Windows

Retention time windows are established and maintained according to procedures outlined in EPA Method 8000, Section 7.5. Three times the standard deviation of the retention time determined from the calibration solutions is used to calculate a window size.

4.2.4 Sample Analysis

AH analyses are initiated with a calibration check, followed by 6-8 samples, and ending with a calibration check. If the response factor for any analyte in the calibration check fails to meet the criteria established in Section 4.2.2, the instrument is recalibrated. All samples that were injected after the standard exceeded the criteria must be reinjected or recalculated based on the analysts review of the data.

Sample injections of 1 to 4 µL are made with an autosampling device.

If the response for any peak exceeds the highest calibration solution, the extract is diluted and reanalyzed.

4.2.5 Calculations

Calculations are based on the methods of internal standards. The general formula for calculating AH is found in Section 7.8.2 of EPA SW-846 Method 8000. See Section 6.1 of this method for details of the calculations. Analyte concentrations can be reported as corrected or uncorrected for the surrogate recoveries.

5.0 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) REQUIREMENTS

5.1 Initial Calibration and Continuing Calibration Checks

Prior to the analyses, a five-point response factor calibration curve establishes the linear range of the detector.

Each calibration standard is analyzed and the response factor (RF) of each compound at each concentration level is calculated from the area of the peak and the gravimetric concentration.

The following formula is used to calculate the response factors of the internal standard relative to each of the calibration standards.

$$RF = (A_S C_{IS}) / (A_{IS} C_S)$$

where:

A_s = Area for the analyte to be measured.
A_{is} = Area for the internal standard (deuterated n-C_{16}).
C_{is} = Concentration of the internal standard (ng/mL) (deuterated n-C_{16}).
C_s = Concentration of the analyte to be measured (ng/mL).

For every 8-10 sample analyses or at least once daily, the response factor for each compound of interest is determined relative to the internal standard.

The daily response factor for each compound is compared to the initial calibration curve. The percent difference is calculated using the following equation:

$$\text{Percent Difference} = \frac{\text{RFI - RFC}}{\text{RFI}} \times 100$$

where:

RFI = Average response factor from initial calibration.

RFC = Response factor from current verification check standard.

If the average daily response factors for all analytes is within ±15 percent of the corresponding calibration curve value, the analysis may proceed. If, for any individual analyte, the daily response factor exceeds ±25 percent of the corresponding calibration curve value, a five-point calibration curve must be repeated for that compound prior to the analysis of the samples. All samples are calculated from the initial calibration.

5.2 Method Blank Analysis

An acceptable method blank analysis does not contain any target compound at concentration 3 times greater than the MDL. If the method blank does not meet these criteria, the analytical system is out of control and the source of the contamination must be investigated, corrective measures taken, and documented before further sample analysis proceeds.

5.3 Surrogate Compound Analysis

All samples and quality control samples are spiked with deuterated n-C_{12}, C_{20}, C_{24} and C_{30}. The surrogate solution will be spiked into the sample prior to extraction to measure individual sample matrix effects associated with sample preparation and analysis.

The laboratory will take corrective action whenever the recovery of deuterated n-C_{12}, C_{20}, C_{24} and C_{30} is outside of 40 to 120 percent for water, sediment and tissue matrices.

The following corrective action will be taken when an out of control event occurs:

a. Calculations are checked to assure that no errors have been made.

b. The internal standard and surrogate solutions are checked for degradation, contamination, etc., and instrument performance is checked.

c. If the surrogate could not be measured because the sample required a dilution, no corrective action is required. The surrogate recovery is properly annotated.

d. If the steps above fail to reveal a problem, the sample or extract is reanalyzed. If reanalysis of the extract yields surrogate recoveries within the stated limits, then the reanalysis data is reported. If upon reinjection QA criteria are still violated, the sample will be submitted for re-extraction if sufficient sample is available. If the sample was completely consumed, the data will be reported but designated as outside the QA criteria.

5.4 Matrix Spike Analysis

The laboratory spikes and analyzes a matrix spike and a matrix spike duplicate (MS/MSD) every 20 samples or with every sample set, which ever is more frequent. A sample is randomly chosen, split into three subsamples and two subsamples are fortified with the matrix spike. The compounds and the spiking levels are presented in Table 1. The acceptable matrix spike recovery criteria for water, sediment and tissue analysis are:

- The average recoveries for all compounds must fall between 40 and 120 percent.

If the matrix spike criteria are not met, the matrix spike will be reinjected on the GC. If the reinjected matrix spike analysis meets the criteria, then the reanalysis data is reported. If not, the entire batch of samples are submitted for re-extraction if sufficient sample is available. If the sample was completely consumed the data will be reported but designated as outside the QA criteria.

5.5 Method Detection Limit

The method detection limit is determined following the procedures outlined in Federal Register (1984), Vol. 49, No. 209: 198- 199.

5.6 GC Resolution

The target compounds, and internal standard must be resolved from one another and from interfering compounds.

5.7 Reference Sample Analysis

When available, reference crude oil will be analyzed for AH. One sample will be analyzed per batch of samples, and the results will be used to establish laboratory QC charts. The result should agree within ±25% of the mean of the previously reported data. The data produced are used to construct control charts.

6.0 CALCULATIONS

6.1 AH Calculations

All calculations are based on the methods of internal standards from Section 7.8.2 of EPA SW-846 Method 8000. Values can be reported as corrected or uncorrected for surrogate recoveries:

- RF = average of $(A_s \times C_{is})/(A_{is} \times C_s)$

where:

A_s = Area of analyte to be measured
A_{is} = Area of internal standard deuterated n-C_{16}
C_{is} = Concentration of the internal standard deuterated n-C_{16} (µg/mL)
C_s = Concentration of the analyte to be measured (µg/mL).

$$Ce = \frac{(A_s)(I_s)}{(A_{is})(RF)}$$

where:

Ce = Sample extract concentration (µg/mL).
A_s = Area of the analyte to be measured.
A_{is} = Area of the the internal standard (deuterated n-C_{16}).
I_s = Amount of internal standard added to each extract divided by the final extract volume (Ve).

The actual sample concentration (C) for each compound is calculated by the following formula:

$$C = (Ce) \times \frac{V_e}{V_s}$$

where:

C = Concentration in sample (µg/L or g).
V_E = The final extract volume (mL).
V_s = The original volume of sample extracted (L or g).

The calculated value is then corrected to one hundred percent recovery based on the surrogate recovery.

6.2 UCM Calculations

- UCM µg/(L or g): = $(A_c \times C_{is} \times D)/(A_{is} \times RF \times S)$

where:

A_c = The corrected area of the sample chromatogram. A_c = (total resolved + unresolved area) minus the total area of all peaks integrated.
C_{is} = µg of internal standard (I.S.) deuterated n-C_{16} added to the extract
D = Dilution factor (if any)
A_{is} = Area response of the I.S. deuterated n-C_{16}
RF = Average response factor of all analytes in the calibration standard
S = Amount of sample extracted--in L for water, in g (wet weight) for sediment or tissue samples.

6.3 Calculation Notes

6.3.1 To each sample, a specific amount of surrogate is added. The recovery of this surrogate is monitored in each sample using the response of the I.S. that is added to the final extract.

$$\text{Percent SUR recovery} = (A_{SUR} \times C_{IS})/(C_{SUR} \times A_{IS} \times RF_{SUR})$$

where:

A_{IS} = Area of deuterated n-C_{16}
A_{SUR} = Area of deuterated n-C_{12}, C_{20}, C_{24}, C_{30}
C_{SUR} = µg of deuterated n-C_{12}, C_{20}, C_{24}, C_{30} added to the sample
C_{IS} = µg of deuterated n-C_{16} added to the sample extract
RF_{SUR} = Response factor for n-C_{12}, C_{20}, C_{24}, C_{30}.

Analyte concentrations can be reported as corrected or uncorrected for surrogate recoveries.

6.3.2 The saturated hydrocarbons n-C_{10} through n-C_{14} may not be quantitatively recovered by the method due to volatility. If the concentrations of individual n-alkanes, n-C_{10} through n-C_{14}, are corrected for the recovery of the surrogate deuterated n-C_{12} precision is effected. Total UCM is determined from n-C_{10} to n-C_{34}. The UCM concentration is an estimate based on the average response factor of the n-alkane calibration standards.

7.0 REPORTING

7.1 Reporting Units

Units are reported in µg/L for water and ng/g for sediments (wet weight) and ng/g for biological tissue (wet weight).

7.2 Minimum Method Performance Criteria

The minimum method performance standard for water is detection of 10 µg/L for the UCM and 0.01 µg/L for individual normal alkane and isoprenoid hydrocarbon compounds. Criteria for sediments (on a wet

weight basis) are 10,000 ng/g for the UCM, and 5 ng/g for individual alkane and isoprenoid hydrocarbon compounds. The minimum method performance standard for biological tissue (on a wet weight basis) is 10,000 ng/g for the UCM and 10 ng/g for individual alkane and isoprenoid hydrocarbon compounds.

7.3 Significant Figures

Results are reported to three (3) significant figures.

7.4 Surrogate Recovery

Surrogate recoveries are reported for every sample analyzed.

7.5 Matrix Spike

Matrix spike recoveries are reported for each batch of samples analyzed.

7.6 Reference Materials

When available the results of the analysis of the crude oil standard reference materials is reported for each batch of samples analyzed.

Note: The effective minimum performance standard can be adjusted by decreasing final sample volume, increasing sample amount and/or increasing volume injected on the GC-FID or GC/MS. Our experience suggests that UCM should be reported in µg/g.

TOTAL AMMONIA--KJELDAHL METHOD

1.0 PROCEDURE

1.1 Setup

(a) Squirt a few mLs of Di (Nanopure in all cases) into 800 mL Kjeldahl flask to help break-up soil particles.

(b) Weight 1.00 gm of soil or slude into flask.

(c) Wash down sides of flask with Di.

(d) Add 50 mLs of digestion reagent.

(e) Add boiling chips if deemed necessary.

1.2 Digestion

(f) Boil briskly on Kjeldahl heaters, under hood or equivalent, until solution turns clear or straw-colored (orange from heater can be seen clearly).

(g) Cool and add approximately 50 mLs Di.

(h) Swirl until precipitate is suspended.

(i) Put contents into 250 mL volumetric and bring to volume.

(j) Save approximately 80-90 mLs in solo cup and analyze with NH_4 probe.

1.3 Reagents

Digestion reagent--add in following order.

(k) Approximately 1300 mLs Di in 2 liter volumetric flask.

(l) 408 mLs concentrated H_2SO_4.

(m) 4.00 gm Mercuric Oxide--red power (HgO).

(n) 268 gm Potassium Sulfate (K_2SO_4).

(o) Dilute to 2 liter.

Standard Methods for the Examination of Water and Waste Water. 16th Ed. 1985. Method 420A, pg. 408. Adapted for use with soils, sediments and sludes.

DIGESTION OF SEDIMENT FOR TRACE METAL ANALYSIS

1.0 INTRODUCTION

Sediments have natural background levels of trace metals that vary widely due to variations in mineralogy and chemistry of source materials and variations in geological and geochemical processes which can deplete or enrich a given sediment. For example, sediments resulting from the weathering of mafic rocks are enriched in Ni, Cu and other trace metals compared to sediments from felsic (granitic) sources. At the same time, fine grained sediment is commonly enriched in trace metals compared to coarse-grained sediment, and sediment rich in organic matter usually contains higher trace metal concentrations than does organic matter poor sediment. Of course, sediment can also vary in trace metal content due to variable inputs by man. Anthropogenic increases in trace metal loads are identified by examining temporal and geographical distribution patterns in relation to known or suspected sources of pollutant metals, while considering those factors (grain size, organic content, etc.) which can affect natural variability.

A method is described herein for the preparation of bottom sediment samples for trace metal analysis by atomic absorption spectrophotometry (AAS). Before samples can be analyzed by AAS methods in use in this laboratory, they must be converted from solid to liquid form. Wet sediment is homogenized in its container, and an aliquot is freeze dried and homogenized to a fine powder. Approximately 0.20 to 0.25 g of powdered sediment is weighed into a Teflon reaction vessel and 3 mL of HNO_3 are added. The vessel is heated in a 130°C oven for 24 hrs. Hydrofluoric acid (2 mL) is added and the reaction vessel is heated again for 24 hrs. Samples are then diluted to a final volume of 20 mL with 5% boric acid and transferred to 1 oz polyethylene bottles for storage until analysis. The samples are then diluted as necessary and analyzed for trace metals by GERG SOP-ST09, ST10, and ST11.

2.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

2.1 Sample Collection

Sediment samples are collected in precleaned glass jars or plastic bags, and frozen in the field.

2.2 Sample Preservation and Storage

Sediment samples are stored at -20°C. Samples are shipped frozen to the laboratory and stored at -20°C until subsampled. After subsampling, excess sample is stored at -20°C. Freeze dried subsamples and sample digests are stored at room temperature.

3.0 INTERFERENCES

Method interferences may be caused by trace metal contaminants associated with reagents, reaction vessels, or sample collection hardware that lead to increased metal concentrations in the digest solution. All materials used in this method are routinely demonstrated to be free from added trace metals by processing procedural blanks identical to samples (2 blanks per 30 samples or each batch, whichever is more frequent).

Matrix interferences may also be caused by compounds other than the analytes of interest in the sediment matrix. Interferences may result in a deviation from reported values in reference materials of a similar sediment type. Each digestion set (not to exceed 30 samples) will contain 2 reference materials of similar type (e.g. mineralogy) and trace metal concentration. Deviation from reported values indicates matrix problems and analytical conditions are adjusted as necessary to remove interferences.

4.0 APPARATUS AND MATERIALS

4.1 Labware and Apparatus

Reaction vessels are cleaned first by soaking in detergent (Micro cleaning solution) for 24 hrs and then rinsed with distilled water. They are then soaked in an acid bath (50% HNO_3) for 24 hrs, rinsed with distilled deionized water, and air dried in a laminar flow hood in a dust free environment. After drying, the reaction vessels are sealed and stored in a dust free environment. Other plasticware used in sample preparation is used only after washing with Micro solution, appropriate acids (either HCl or HNO_3, depending upon resistance to attack), and distilled, deionized water.

The following labware is needed to perform the sediment digestion and dilution procedure:

Mortar and Pestle: To homogenize sample.

Reaction Vessels: Savillex 50 mL Teflon reaction vessels or equivalent.

Oven: Heated to 130°-135°C.

Disposable Plastic Transfer Pipets: 1 mL.

Balance: Top loading with accuracy of 0.01 g.

Analytical Balance: With an accuracy of 0.0001 g.

Screw Top Bottles: 1 oz Nalgene or equivalent.

Repipet: To add boric acid for dilution, 10 mL capacity.

Microliter Pipets: 1000-, 500-, 300-, 200-, 100-, 50-, 25- and 10 µl capacity.

Note: Microliter pipets must be calibrated.

4.2 Reagents

The procedure requires the following:

Reagent Water: Reagent water contains no analytes above the method detection limit. Reagent water is produced by subboiling redistillation of water in a quartz still.

Nitric Acid: Baker Ultrex Grade or equivalent, stored in Teflon bottle.

Hyrdrofluoric Acid: Baker analyzed or equivalent.

Boric Acid: Ultrex grade or equivalent.

5.0 PROCEDURES

All sediment samples are freeze dried and mechanically powdered with a mortar and pestle prior to digestion.

5.1 Preparation of Samples

When samples are received frozen, they are thawed, and excess water is aspirated from the surface. The samples are mixed with a plastic spatula and subsampled into polyethylene vials. The original sample container is resealed and refrozen and the subsample is freeze dried and ground.

5.2 Digestion and Extraction

5.2.1 Approximately 0.20 g of dry powdered sediment is weighed to the nearest 0.1 mg and placed in a preweighed reaction vessel. Three mL of Ultrex HNO_3 is added, the lid is tightened to 18 ft lbs torque, and the vessel is placed into the 130°C oven for 24 hrs.

5.2.2 Vessels are removed from the oven, allowed to cool, and opened to vent excess pressure. Two mL of HF are added, the lid is tightened, and the reaction vessel is returned to the oven for 24 hrs.

5.2.3 Vessels are removed from the oven, allowed to cool, and opened to vent excess pressure. Seventeen mL of 5% boric acid solution are added using a repipet, the lids are retightened and the reaction vessel is returned to the oven for 24 hrs to aid dissolution.

5.2.4 The solution is transferred from the reaction vessels to 1 oz Nalgene sample bottles. Samples are ready to be analyzed by GERG SOP-ST09, ST10, and ST11.

6.0 QUALITY CONTROL

Quality control samples are processed in a manner identical to actual samples.

6.1 Method Blanks

Two method blanks are run with every 30 samples or with every sample set, whichever is more frequent. Blank levels should be no more than 2x method detection limit (MDL). If blank levels for any analyte are above the 2x MDL, samples analyzed in that sample set are redigested. If insufficient sample is available, the data are reported with a blank correction and flagged as such.

6.2 Reference Materials

Sediment reference materials, as closely matching the sample set as available, are run with each sample set. Two different materials are run to maximize the possible interferences seen. Control charts for these analyses are then established. Criteria for reference material performance can be found in GERG SOP-ST09, ST10, and ST11.

7.0 REPORTING AND PERFORMANCE

7.1 Reporting units for trace metals are generally µg/g (dry weight). Several elements occurring at higher concentration are reported as % dry weight (e.g. Al, Fe, Si).

7.2 Results from sample processing and digestion are used in subsequent analyses, and are expressed as a "digestion dilution factor", having units of mL/g.

7.3 Trace metal performance standards are determined for each individual analyte and are discussed in GERG SOP-ST09, ST10, and ST11.

ANALYSIS OF TRACE METALS BY FLAME ATOMIC ABSORPTION

1.0 INTRODUCTION

Flame atomic absorption spectrophotometry (FAAS) relies on a flame to provide the heat necessary to evaporate the solvent (water) and break molecular bonds in order to produce a cloud of free atoms in the path of an absorption spectrophotometer. In general, the method is rapid, sensitive, and free from inter-element interferences.

Samples are analyzed by FAAS when concentrations are high enough to give absorbance readings greater than 0.010 absorbance unit. When concentrations are lower, the samples must be run by a more sensitive technique (e.g. GFAAS, CVAAS) in order to obtain something other than "<" readings.

The quantitative methods described in this document are for the analysis of tissue or sediments prepared according to SOP-ST07 or ST08, respectively. Sample collection, preservation, storage and digestion are described in these documents.

2.0 APPARATUS AND LABWARE

2.1 Apparatus

2.1.1 FAAS

The instrument utilized in this method is a Perkin-Elmer Model 306 atomic absorption spectrophotometer equipped with a deuterium (D_2) background corrector. Most elements of interest can be analyzed using an air-acetylene flame and a 3 inch burner head. For elements requiring higher flame temperatures for complete atomization (e.g. Al), a nitrous oxide-acetylene flame is used with a 2 inch burner head.

2.1.3 Hollow Cathode Lamps

The use of special light sources and careful wavelength selection permits the specific determination of one element in the presence of others. Hollow cathode lamps consist of a sealed glass cylinder filled with an inert gas, an anode, a cathode, and a end window. The cathode is a hollow cylinder of the element whose spectrum is to be produced.

2.1.4 Electrodeless Discharge Lamps

Electrodeless discharge lamps (EDL) are typically more intense and usually provide better sensitivity than hollow cathode lamps. EDLs consist of the element of interest or a salt sealed in a quartz bulb containing an inert atmosphere. The bulb is contained in a ceramic holder on which an RF coil is wound.

2.2 Labware

The following labware is needed to preform the analytical procedure:

Balance: Top loading with accuracy of 0.01 g.

Microliter Pipets: 1000-, 500-, 300-, 200-, 100-, 50-, 25- and 10 µl capacity.

Note: Microliter pipets must be calibrated.

3.0 REAGENTS

The procedure requires the following:

Reagent Water: Reagent water contains no analytes above the method detection limit. Reagent water is produced by passing house-distilled water through a deionizing cartridge.

Nitric Acid: Baker Ultrex Grade or equivalent, stored in Teflon bottle.

Calibration Standard: The calibration solution is derived from commercially available reference standards diluted in nitric acid (for most elements). A maximum concentration is chosen from either the expected sample concentrations or the element's linear detection range, whichever is smaller, and a series of working standards is made to span the range from this concentration to the blank. Each element's appropriate calibration standard concentrations are given along with standard operating conditions in Section 4.1.

Matrix Recovery Spiking Solution: The matrix spiking solution customarily is one of the calibration standard solutions. The goal in matrix recovery spiking is to add a spike that increases analyte concentration by at least 20%, while leaving sample matrix largely unaffected. If the ratio of sample to spike volumes is 1:0.2, in order to achieve a final concentration that is 20% higher than the sample concentration, the ratio of spike

solution:sample concentration must be at least 2.2. Care must be taken that the spiked sample is analyzed within the linear range.

4.0 PROCEDURES

All tissue or sediment samples are collected, preserved, stored and digested as described by GERG SOP-ST07 or ST08, respectively.

4.1 Standard Elemental Conditions Instrumental conditions and typical calibration standards are as follows:

Element	Source	Wavelength	Slit	Flame	High Standard	Low Standard
Al	HCL	309.3	0.7	N_2O/acet.	50	15
Ca	HCL	422.7	14.	air/acet.	7	2
Cd	EDL	228.8	0.7	air/acet.	2	0.7
Cr	HCL	357.9	0.7	air/acet.	5	1.5
Cu	HCL	324.7	0.7	air/acet.	5	1.5
Fe	HCL	248.3	0.2	air/acet.	5	1.5
K	HCL	766.5	14.	air/acet.	2	0.7
Mg	HCL	285.2	0.7	air/acet.	0.5	0.15
Mn	HCL	279.5	0.2	air/acet.	3	1
Na	HCL	589	14.	air/acet.	1	0.3
Ni	HCL	232.0	0.2	air/acet.	5	1.5
Pb	EDL	283.3	0.7	air/acet.	20	7
Si	HCL	251.6	0.2	N_2O/acet.	150	50
Sr	HCL	460.7	0.4	air/acet.	5	1.5
V	HCL	318	0.7	air/acet.	150	50
Zn	HCL	213.9	0.7	air/acet.	1	0.3

where HCL = hollow cathode lamp,
EDL = electrodeless discharge lamp,
wavelength and slit widths are in nm,
air/acet = air-acetylene flame,
N_2O/acet = nitrous oxide-acetylene flame,
Calibration standards are in units of ppm (µg/mL); typically, at least four equally spaced calibration standards are used, including the blank.

4.2 Order of Analysis

Samples are analyzed as follows:

1. Calibration standards are run. Sensitivity is checked against manufacturer's reports and historical data to verify proper operation.

2. A reference material is analyzed, and its concentration determined and checked against reported values.

3. A spike into the reference material is run, to examine possible interferences.

4. Samples are analyzed.

5. After every 10th sample, a calibration check is made to determine whether instrumental sensitivity is stable.

5.0 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

Quality control samples are processed in a manner identical to actual samples.

5.1 Two method blanks are run with every 30 samples or with every sample set, whichever is more frequent. Blank levels should be no more than 2x method detection limit (MDL). If blank levels for any analyte are above the 2x MDL, samples analyzed in that sample set are redigested. If insufficient sample is available, the data are reported with a blank correction and flagged as such.

5.2 Reference Materials: Reference materials analyzed with the samples are matched as closely as possible to sample composition and expected trace metal concentrations, and the results of these analyses are incorporated into control charts. Reference materials currently in use include:

Tissue samples:

DORM-1 (NRC, Canada),
DOLT-1 (NRC, Canada), and
MUSSEL No. 6 (NIES, Japan)

Sediment samples:

BCSS-1 (NRC, Canada),
MESS-1 (NRC, Canada),
Estuarine sediment, #1646 (NBS, U.S.), and
HS-2 (TAMU house reference standard).

5.3 Matrix Spikes

Matrix spikes are used to investigate possible interferences which may result in either signal enhancement or suppression. Spiked and unspiked sample concentrations are compared and spike recovery is calculated according to the equation:

$$\text{Spike recovery (\%)} = \frac{C_{\text{spkd spl}}V_{\text{spkd spl}} - C_{\text{spl}}V_{\text{spl}}}{C_{\text{spk}}V_{\text{spk}}} \times 100$$

where $C_{\text{spkd spl}}$ = the concentration observed in the spiked sample,
$V_{\text{spkd spl}}$ = the volume of the spiked sample = $V_{\text{spl}} + V_{\text{spk}}$,
C_{spl} = the concentration observed in the unspiked sample,
V_{spl} = the volume of sample used in making the spiked sample,
C_{spk} = the concentration of the spiking solution, and
V_{spk} = the volume of spike solution used in making the spiked sample.

5.4 Duplicate Analysis

Duplicate samples are run with every 20 samples or with every sample set. Duplicates should be within ±20% for low-level samples, and ±10% for higher samples. Inhomogeneous samples may result in greater variability between duplicates. Experience has indicated that reference materials are more homogeneous than are samples, and thus comparison of a) reference material duplicate analyses, b) sample duplicate analyses and c) duplicate analyses from single digestion solutions gives an indication of a) total analytical variability (i.e. processing + instrumental variability), b) the sum of analytical variability and natural sample inhomogeneity, and c) instrumental variability.

5.5 Recalibration

The entire suite of calibration standards is run at the beginning and end of each run. In addition, one or more calibration standards are run after every 10 samples in order to observe instrumental drift and resultant

change in sensitivity. Where drift is apparent, it can frequently be resolved by adjusting the wavelength, checking for an obstruction in the capillary tubing leading to the nebulizer, or resetting flame conditions. If these adjustments restore the original sensitivity, samples analyzed following the last acceptable calibration check are reanalyzed. When drift cannot be corrected, samples are calibrated against standards analyzed at the beginning and end of each group of 10 samples. When these standards differ significantly from one another, the samples are rerun.

6.0 CALCULATIONS

Calculations are based upon measurements of absorption peak height of samples, standards, and blanks, and are based on the following formula:

$$\text{Concentration (ppm)} = [(a + bAbs_{spl}) \times DF_{spl} - (a + bAbs_{PB})] \times DF_{dig'n}$$

where:

"a" and "b" are the intercept and slope of the line obtained from the calibration standards,

Abs_{spl} is the sample absorbance,

DF_{spl} is the dilution factor needed to dilute samples to a concentration where they can be analyzed within the linear range of the instrument,

Abs_{spl} is the absorbance of the procedural blanks analyzed with the current batch of samples, and

$DF_{dig'n}$ is the dilution factor resulting from digestion of the samples, with units of mL/g.

7.0 REPORTING AND PERFORMANCE

7.1 Reporting Units

Reporting units are µg/g (dry weight).

7.2 Minimum Method Performance Criteria

The minimum method performance standard for the method is dependent upon the dilution factor resulting from digestion of the tissue or sediment sample and on the sensitivity of the technique for each element. General requirements for acceptable instrumental performance include

instrumental sensitivity that is no less than 80% of that reported by the manufacturer or from historical records (instrumental sensitivities listed in section 4.1), so that minimum performance criteria, given a sample digestion dilution factor of ~100, are 80 x the reported instrumental criteria.

7.3 Significant Figures

Results are reported to the number of significant figures that matches the number of such figures in the absorption reading. Samples with absorption less than 0.010 can be reported with only 1 significant figure, samples with absorbance equal to or greater than 0.010 and less than 0.100 can have only two significant figures, and samples with absorbance greater than or equal to 0.100 are reported with three significant figures.

7.4 Duplicate Analyses

All duplicate analyses are reported. Duplicate analyses are run with at least every 20 samples.

7.5 Reference Materials

Reference materials analyzed with the samples are matched as closely as possible to sample composition and expected trace metal concentration. Reference materials currently in use include:

Tissue samples:

DORM-1 (NRC, Canada),
DOLT-1 (NRC, Canada), and
MUSSEL No. 6 (NIES, Japan).

Sediment samples:

BCSS-1 (NRC, Canada),
MESS-1 (NRC, Canada),
Estuarine sediment, #1646 (NBS, U.S.), and
HS-2 (TAMU house reference standard).

ANALYSIS OF TRACE METALS BY GRAPHITE FURNACE ATOMIC ABSORPTION

1.0 INTRODUCTION

Graphite furnace atomic absorption spectrophotometry (GFAAS) relies on the electrical resistance heating generated by passing an electrical current through a graphite tube to evaporate solvent (water), remove interfering species, and finally atomize the analyte into the light path of an absorption spectrophotometer. This technique is roughly two orders of magnitude more sensitive than FAAS, primarily because the whole sample injected into the graphite tube is analyzed (as opposed to 10% in the case of FAAS), and because the absence of a flame results in a better signal-to-noise ratio. However, the GFAAS technique is much slower, requiring up to several minutes for individual analyses, and is generally much more susceptible to interferences.

Samples are analyzed by GFAAS when their concentrations are below the working range of FAAS, or when sample volume is small. Tissue and sediment digests result in sample volumes of roughly 20 mL or more, so that for these analyses GFAAS is generally used to obtain low detection limits.

The quantitative methods described in this document are for the analyses of tissue or sediments prepared according to SOP-ST07 or ST08, respectively. Sample collection, preservation, storage and digestion are described in these documents.

2.0 APPARATUS AND LABWARE

2.1 Apparatus

2.1.1 GFAAS

The GFAAS instrument used in this laboratory is a Perkin-Elmer Zeeman 3030 equipped with a HGA 600 furnace capable of an almost infinite range of temperatures, heating rates and holding times.

2.1.2 Autosampler

The GFAAS is equipped with an AS-60 autosampler having 40 sample positions and allowing for delivery of sample and matrix modifier volumes from 1-99 µl.

2.1.3 Hollow Cathode Lamps

The use of special light sources and careful wavelength selection permits the specific determination of one element in the presence of others. Hollow cathode lamps consist of a sealed glass cylinder filled with an inert gas, an anode, a cathode, and a end window. The cathode is a hollow cylinder of the element whose spectrum is to be produced.

2.1.4 Electrodeless Discharge Lamps

Electrodeless discharge lamps (EDL) are typically more intense and usually provide better sensitivity than hollow cathode lamps EDLs consist of the element of interest or a salt sealed in a quartz bulb containing an inert atmosphere. The bulb is contained in a ceramic holder on which an RF coil is wound.

2.2 Labware

The following labware is needed to perform the analytical procedure:

Balance: Top loading with accuracy of 0.01 g.

Autosampler Cups: 2.0 mL polystyrene autosampler cups.

Microliter Pipets: 1000-, 500-, 300-, 200-, 100-, 50-, 25- and 10 µl capacity.

Note: Microliter pipets must be calibrated.

3.0 REAGENTS

The procedure requires the following:

Reagent Water: Reagent water contains no analytes above the method detection limit. Reagent water is produced by redistilling water in a quartz still.

Nitric Acid: Baker Ultrex Grade or equivalent, stored in Teflon bottle.

Calibration Standard: The calibration solution is derived from a commercially available reference standard diluted in nitric acid. A concentration is chosen to fall at the upper end of either the expected sample levels or the element's linear detection range, whichever is smaller.

Each element's appropriate calibration standard concentrations are given along with standard operating conditions in Section 4.1.

Matrix Recovery Spiking Solution: The matrix spiking solution customarily is the Calibration Standard solution. In cases where addition of a 25% volume will not raise the sample concentration more than 20% another more concentrated solution is needed. The concentration of this solution is determined such that addition of up to a 25% volume will cause at least a 20% increase in observed concentration with care taken not to exceed the linear range of analysis.

Matrix modifiers: The technique of GFAAS has been greatly advanced by the use of several matrix modifiers which remove or greatly diminish interferences from sample matrix. The modifiers assist in the analysis by either increasing the volatility of an interferent, or by increasing the analyte's thermal stability so that the sample may be charred at a higher temperature. Modifiers used for this purpose are listed in Section 4.1.

4.0 PROCEDURES

All tissue or sediment samples are collected, preserved, stored and digested as described by GERG SOP-ST07 or ST08, respectively.

4.1 Standard Elemental Conditions

Instrumental operating conditions, matrix modifiers, and expected sensitivities are as follows:

Element	Source	Wavelength	Slit	Site	Matrix Modifier	Char. mass
Ag	HCL	328.1	0.7	P	0.015 mg Pd + 0.01 mg $Mg(NO_3)_2$	1.5
As	EDL	193.7	0.7	P	0.015 mg Pd + 0.01 mg $Mg(NO_3)_2$	15.
		197	0.7	P	0.015 mg Pd + 0.01 mg $Mg(NO_3)_2$	30.
Cd	EDL	228.8	0.7	P	0.2 mg PO_4 + 0.01 mg $Mg(NO_3)_2$	0.35
Cr	HCL	357.9	0.7	P	0.05 mg $Mg(NO_3)_2$	3.3
Cu	HCL	324.7	0.7	P	0.015 mg Pd + 0.01 mg $Mg(NO_3)_2$	8.0
Fe	HCL	248.3	0.2	P	0.05 mg $Mg(NO_3)_2$	5.0
Mn	HCL	279.5	0.2	P	0.05 mg $Mg(NO_3)_2$	2.2
Mo	HCL	313.3	0.7	W		9.0
Ni	HCL	232.0	0.2	P		13.0
Pb	EDL	283.3	0.7	P	0.2 mg PO_4 +	12.0

Sb	EDL	217.6	0.7	P	0.01 mg $Mg(NO_3)_2$ 0.015 mg Pd + 0.01 mg $Mg(NO_3)_2$	22.0
Se	EDL	196.0	0.7	P	0.01 mg $Mg(NO_3)_2$ 0.015 mg Pd + 0.01 mg $Mg(NO_3)_2$	28.0
Sn	EDL	286.3	0.7	P	0.01 mg $Mg(NO_3)_2$ 0.015 mg Pd + 0.01 mg $Mg(NO_3)_2$	24.0
V	HCL	318.4	0.7	W	0.05 mg $Mg(NO_3)_2$	40.0
Zn	HCL	213.9	0.7	P	0.006 mg $Mg(NO_3)_2$	0.45

where HCL = hollow cathode lamp,
EDL = electrodeless discharge lamp,
Wavelength and slit width are in nm,
Under Site, "P" and "W" refer to "platform" and "wall" as the site if sample deposition, respectively,
The characteristic mass is the mass of the analyte, in picograms, expected to result in a peak area of 0.0044 Abs-sec.

Calibration Standards for Graphite Furnace

Element	Concentration (ppb) Low	Mid	High
Ag	1.5	3.0	4.5
As	20	40	60
Cd	0.4	0.8	1.2
Dr	4.0	8.0	12.0
Cu	10	20	30
Fe	5	10	15
Mn	2.5	5.0	7.5
Mo	10	20	30
Ni	15	30	45
Pb	15	30	45
Sb	45	90	135
Se	35	70	105
Sn	25	50	75
V	45	90	135
Zn	0.1	0.2	0.3

4.2 Sample Order

Samples are placed in the autosampler as follows:

Position	Contents
1	Matrix Modifier
2-4	Calibration Standards
5	Reference Material
6	Matrix Spike in Reference Material
7	Procedural Blank
8-17	Samples
18	Matrix Spike into Sample 17
19-29	Samples
30	Matrix Spike into Sample 29
31-37	Samples
38	Procedural Blank
39	Reference Material
40	Duplicate run of sample in 8

5.0 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

Quality control samples are processed in a manner identical to actual samples.

5.1 Two method blanks are run with every 30 samples or with every sample set, whichever is more frequent. Blank levels should be no more than 2x method detection limit (MDL). If blank levels for any analyte are above the 2x MDL, samples analyzed in that sample set should be redigested. If insufficient sample is available, the data will be reported with a blank correction and flagged as such.

5.2 Reference Materials

Reference materials analyzed with the samples are matched as closely as possible to sample composition and expected trace metal concentrations, and the results of these analyses are incorporated into control charts. Reference materials currently in use include:

Tissue samples:

DORM-1 (NRC, Canada),
DOLT-1 (NRC, Canada), and
MUSSEL No. 6 (NIES, Japan).

Sediment samples:

BCSS-1 (NRC, Canada),
MESS-1 (NRC, Canada),
Estuarine sediment, #1646 (NBS, U.S.), and
HS-2 (TAMU house reference standard).

5.3 Matrix Spikes

Matrix spikes are used to investigate possible interferences which may result in either signal enhancement or suppression. Spiked and unspiked sample concentrations are compared and spike recovery is calculated according to the equation:

$$\text{Spike recovery (\%)} = \frac{C_{spkd\ spl}V_{spkd\ spl} - C_{spl}V_{spl}}{C_{spk}V_{spk}} \times 100$$

where $C_{spkd\ spl}$ = the concentration observed in the spiked sample,
$V_{spkd\ spl}$ = the volume of the spiked sample = $V_{spl} + V_{spk}$,
C_{spl} = the concentration observed in the unspiked sample,
V_{spl} = the volume of sample used in making the spiked sample,
C_{spk} = the concentration of the spiking solution, and
V_{spk} = the volume of spike solution used in making the spiked sample.

5.4 Duplicate Analysis

Duplicate samples are run with every 20 samples or with every sample set. Duplicates should be within ±20% for low-level samples, and ±10% for higher samples. Inhomogeneous samples may result in greater variability between duplicates. Experience has indicated that reference materials are more homogeneous than are samples, and thus comparison of a) reference material duplicate analyses, b) sample duplicate analyses and c) duplicate analyses from single digestion solutions gives an indication of a) total analytical variability (i.e. processing + instrumental variability), b) the sum of analytical variability and natural sample inhomogeneity, and c) instrumental variability.

5.5 Recalibration

The entire set of calibration standards is run at the beginning of the analysis, and is rerun after autosampler positions 16, 28, and 40 have been analyzed, or after every 12 samples.

6.0 CALCULATIONS

Sample concentrations are determined from the Z-3030 calibration results and from the dilution factors involved in instrumental analysis and sample digestion according to the following equation:

$$\text{Concentration (ppm)} = [Conc_{spl} \times DF_{spl} - Conc_{PB}] \times DF_{dig'n} \div 1000$$

where $Conc_{spl}$ = the concentration observed in the sample, in ppb,
$Conc_{PB}$ = the concentration observed in the procedural blanks, in ppb,
DF_{spl} = the dilution factor required to dilute the sample concentration to the working range of the machine,
$DF_{dig'n}$ = the dilution factor resulting from sample digestion, in mL/g.

7.0 REPORTING AND PERFORMANCE

7.1 Reporting Units

Reporting units are µg/g (dry weight).

7.2 Minimum Method Performance Criteria

The minimum method performance standard for the method is dependent upon the dilution factor resulting from digestion of the tissue or sediment sample and on the sensitivity of the technique for each element. General requirements for acceptable instrumental performance include instrumental sensitivity that is no less than 80% of that reported by the manufacturer or from historical records (instrumental characteristic masses listed in Section 4.1), so that minimum performance criteria, given a sample digestion dilution factor of ~100, are 80 x the reported instrumental criteria.

7.3 Significant Figures

Results are reported to the number of significant figures that matches the number of such figures in the absorption reading. Samples with

absorption less than 0.010 can be reported with only 1 significant figure, samples with absorbance equal to or greater than 0.010 and less than 0.100 can have only two significant figures, and samples with absorbance greater than or equal to 0.100 are reported with three significant figures.

7.4 Duplicate Analyses

All duplicate analyses are reported. Duplicate analyses are run at least every 20 samples.

7.5 Reference Materials

Reference materials analyzed with the samples are matched as closely as possible to sample composition and expected trace metal concentration. At least two reference samples are digested and analyzed with each group of samples. Reference materials currently in use include:

Tissue samples:

DORM-1 (NRC, Canada),
DOLT-1 (NRC, Canada), and
MUSSEL No. 6 (NIES, Japan).

Sediment samples:

BCSS-1 (NRC, Canada),
MESS-1 (NRC, Canada),
Estuarine sediment, #1646 (NBS, U.S.), and
HS-2 (TAMU house reference standard).

ANALYSIS OF MERCURY BY COLD-VAPOR ATOMIC ABSORPTION

1.0 INTRODUCTION

Mercury is analyzed by an atomic absorption procedure that differs from flame and graphite furnace AAS in the technique used to produce a cloud of free analyte atoms. Whereas flame and graphite furnace AAS rely on heat to break chemical bonds and to atomize the elements of interest, the cold vapor mercury method, as developed by Hatch and Ott (1968) takes advantage of elemental mercury's high vapor pressure.

In this procedure, divalent mercury (Hg^{++}) in aqueous samples (either water samples or tissue or sediment digests) is reduced to the elemental state (Hg^{o}) by a strong reducing agent (stannous chloride). The fraction of Hg^{o} that enters the gas phase is introduced into an atomic absorption cell, where light produced by a separate mercury vapor lamp is absorbed by the free Hg atoms. The amount of mercury in the sample is determined by comparing light absorption of the sample with that of calibration standards.

The quantitative methods described in this document are for the analyses of tissue or sediments prepared according to SOP-ST07 or ST08, respectively. Sample collection, preservation, storage and digestion are described in these documents.

2.0 APPARATUS AND LABWARE

2.1 Apparatus

2.1.1 Cold Vapor Mercury Analyzer

The cold vapor mercury analyzer used in this laboratory is an LCD Model 1235 uvMonitor equipped with a 30 cm path length absorption cell and operating at the 254 nm wavelength. The instrument is attached to a Houston Instrument Omniscribe chart recorder operating at 10 mV full scale.

2.2 Labware

The following labware is needed to perform the analytical procedure:

Balance: Top loading with accuracy of 0.01 g.

Microliter Pipets: 1000-, 500-, 300-, 200-, 100-, 50-, 25- and 10 µl capacity.

Note: Microliter pipets must be calibrated.

Reaction Flasks: 25 mL glass Erlenmeyer flasks, one required for each analysis.

Rubber Septum Stoppers: To seal mouth of 25 mL glass Erlenmeyer flasks.

Syringe: Disposable 2 cc plastic syringe, fitted with small-bore needle.

3.0 REAGENTS

The procedure requires the following:

Reagent Water: Reagent water contains no analytes above the method detection limit. Reagent water is produced by redistilling water in a quartz still.

Nitric Acid: Baker Ultrex Grade or equivalent, stored in Teflon bottle.

Hydrochloric Acid: Baker Ultrex Grade or equivalent, stored in Teflon bottle or original glass bottle.

Calibration Standard: The calibration solution is comprised of a commercially available reference standard diluted in nitric acid. Our experience has shown that almost all tissue and sediment samples can be analyzed with optimum accuracy and precision at the uvMonitor's "0.02" range setting. This produces a near full scale pen deflection for a solution containing 2 ppb Hg. Therefore, serial dilutions of a 1000 ppm Hg stock solution are made with 0.2 M HNO_3, using polystyrene snap cap vials as containers. The final working standards (≤ 2ppb) must have a small amount of Ultrex grade HCl added (final concentration ~0.01 M HCl) or the solution will deteriorate within a few hours of preparation.

Matrix Recovery Spiking Solution: The matrix spiking solution customarily is the Calibration Standard solution. In cases where addition of a 25% volume will not raise the sample concentration more than 20% another more concentrated solution is needed. The concentration of this solution is determined such that addition of up to a 25% volume will cause at least a 20% increase in observed concentration with care taken not to exceed the linear range of analysis.

Stannous Chloride: A 10% Sn^{++} solution is used to reduce Hg^{++} to Hg^{o}. It is made by adding 10 g $SnCl_2$ to 100 mL of 0.5 N H_2SO_4. Any Hg contamination can be removed by stirring this solution overnight, allowing Hg^{o} to escape to the atmosphere.

4.0 PROCEDURES

All tissue or sediment samples are collected, preserved, stored and digested as described by GERG SOP-ST07 or ST08, respectively.

4.1 Operation

Unlike some cold-vapor procedures that involve the use of a gas stream to strip Hg from the reaction vessel, the technique utilized in this laboratory is essentially a "head-space" technique. A small volume of sample or standard solution is introduced to the 25 cc Erlenmeyer flask, and the mouth is sealed with a rubber septum stopper. The Sn^{++} reductant is injected into the flask with the 2 cc plastic syringe, resulting in the reduction of Hg^{++} to Hg^{o}, and the flask is swirled to produce an equilibrium distribution of between the solution volume and the head space in the flask. Finally, the flask is connected to the uvMonitor by means of a syringe needle, and a large-bore needle that is connected to a water supply is inserted through the septum and forced to the bottom of the flask. A pinch clamp on the water line is opened, and the water entering the flask forces the head space gas, with its Hg^{o}, into the absorption cell.

Operating Steps:

1. Using an Eppendorf pipet, add 1 mL of sample or standard to a clean 25 cc flask.

2. Insert rubber stopper into mouth of flask. Prior to insertion, stopper should have small gauge needle inserted into it to allow air to escape from flask as stopper is inserted. Remove this needle after stopper is in place.

3. Using 2 cc plastic syringe and small gauge needle, inject 10% $SnCl_2$ (three drops) into flask.

4. Swirl flask for 45 seconds to mix solutions and allow exchange of Hg^{o} across the air-water interface.

5. Activate chart recorder.

6. Pierce rubber septum with syringe needle connected to Hg monitor with tygon tubing. Pierce stopper with large gauge needle connected to water supply, and force tip of needle to bottom of flask to minimize turbulence when adding water. Open pinch clamp on water line, and allow water to displace air from the flask until water level is within 0.5 cm of the stopper. Close pinch clamp.

7. Remove needles from stopper. Remove Hg^0 from absorption cell with vacuum. When recorder pen returns to baseline, turn recorder off.

8. Quantitate by measuring peak height in millimeters, and compare with calibration standards analyzed with same starting volume.

5.0 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

Quality control samples are processed in a manner identical to actual samples.

5.1 Method Blanks

Two method blanks are run with every 30 samples or with every sample set, whichever is more frequent.

5.2 Reference Materials

Tissue reference materials, as closely matching the sample set as available, are run with each sample set. Two different materials are run to maximize the possible interferences seen. Control charts for these analyses are then established.

5.3 Reagent Blanks

New batches of digestion acids (HNO_3, HF, $HClO_4$, H_3BO_3) and laboratory water supplies (both distilled/deionized and distilled/sub-boiling quartz-distilled) are routinely analyzed to identify sources of contamination before samples are processed.

5.4 Matrix Spikes

Possible matrix interferences are investigated by performing matrix spike determinations on the samples. A small volume of a Hg standard is added to a portion of the sample, which is then analyzed as above. Matrix spike recovery is considered acceptable when it is within 10% of 100%. If

the recovery is outside these limits, it is repeated and the reanalysis data is reported if it meets the criterion.

5.5 Duplicate Analyses

Duplicate samples are run with every 20 samples or with every sample set. Inhomogeneous samples may result in greater variability between duplicates. Experience has indicated that reference materials are more homogeneous than are samples, and thus comparison of a) reference material duplicate analyses, b) sample duplicate analyses and c) duplicate analyses from single digestion solutions gives an indication of a) total analytical variability (i.e. processing + instrumental variability), b) the sum of analytical variability and natural sample inhomogeneity, and c) instrumental variability.

5.5 Recalibration

Calibration standards are rerun after each 20 samples. If these differ from those run earlier by > 5%, they are rerun. If there is still a difference, the system is checked for leaks, partially blocked syringe needles, etc. Our experience has shown the mercury analyzer to be extremely stable, and that sources of sensitivity changes are generally either flow-related (leaks, clogging) or due to either a standard problem (e.g. introduction of only a minute amount of $SnCl_2$ will lead to a significant loss of Hg from the standard) or to a deteriorated $SnCl_2$ solution.

6.0 CALCULATIONS

Because elemental mercury is distributed between the aqueous and gas phases, it is important that similar volumes of samples and standards are added to the reaction flasks at the beginning of the procedure. Since there is a limited volume available in the flask, the amount of Hg in the gas phase is dependent upon the total amount of Hg available and on the relative volumes of liquid and air in the flask.

Calculations are based upon measurements of peak height of samples, standards, and blanks, and are based on the following formula:

$$\text{Hg (ppm)} = [PH_{spl} \times DF_{Hg} - PB] \times \text{slope} \times DF_{dig'n} \div 1000$$

where

Hg (ppm) is the final mercury concentration in units of μg Hg per gram dry weight of tissue or sediment,

PH_{spl} is the peak height of the sample, in mm,

DF_{Hg} is the dilution factor needed to dilute samples to a concentration where they can be analyzed on the "0.02" range scale (i.e. to a level ~2 ppb)

Slope is the slope of the calibration curve, with units ppb Hg/mm,

PB is the peak height of the procedural blanks analyzed with the current batch of samples, in mm,

$DF_{dig'n}$ is the dilution factor resulting from digestion of the samples, with units of mL/g.

7.0 REPORTING AND PERFORMANCE

7.1 Reporting Units

Reporting units are µg/g (dry weight).

7.2 Minimum Method Performance Criteria

The minimum method performance standard for the method is dependent upon the dilution factor resulting from digestion of the tissue or sediment sample. Assuming a typical dilution factor of 100 and normal blank levels and instrumental sensitivity, the minimum method performance standard is 0.01 ppm Hg in a sample.

7.3 Significant Figures

Results are reported to two (2) significant figures for samples with Hg peaks < 100 mm, and to three (3) significant figures for samples with Hg peaks ≥ 100 mm.

7.4 Duplicate Analyses

All duplicate analyses are reported. Duplicate analyses are run at least every 20 samples.

7.5 Reference Materials

Reference materials analyzed with the samples are matched as closely as possible to sample composition and expected Hg concentration. Reference materials currently in use include:

Tissue samples:

DORM-1 (NRC, Canada),
DOLT-1 (NRC, Canada), and
MUSSEL No. 6 (NIES, Japan).

Sediment samples:

BCSS-1 (NRC, Canada),
MESS-1 (NRC, Canada),
Estuarine sediment, #1646 (NBS, U.S.), and
HS-2 (TAMU house reference standard).

QUANTITATIVE DETERMINATION OF SELECTED TRACE ELEMENTS BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA)

1.0 INTRODUCTION

This method determines the total concentration of antimony (Sb), barium (Ba), cerium (Ce), cobalt (Co), chromium (Cr), iron (Fe), hafnium (Hf), rubidium (Rb), scandium (Sc) and thorium (Th) in dry sediment.

2.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

2.1 Sample Collection

Sediment samples are collected in pre-cleaned glass jars or plastic bags, and frozen in the field.

2.2 Sample Preservation and Storage

Sediment samples are stored at -20°C. Samples should be shipped frozen to the lab and stored at -20°C until subsampled. After subsampling, excess sample is stored at -20°C. Freeze dried subsamples and sample digests are stored at room temperature.

3.0 INTERFERENCES

Contamination of sediment during sample preparation and handling is the primary source of interferences for INAA. Methods used to avoid contamination are discussed in section 5 below. Spectral interferences during gamma-ray spectrometry are avoided by using gamma-ray energies which exhibit no spectral interferences in typical sediment samples.

4.0 APPARATUS AND MATERIALS

4.1 Labware and Apparatus

Sample polyvials (2/5 dram) are cleaned by soaking in a 1:1 solution of concentrated nitric acid and distilled water for 24 hours. The polyvials are then rinsed with reagent grade acetone, covered with lintless filter paper and allowed to dry at room temperature. Dry polyvials are stored in sealed plastic bags until used.

The following labware is needed to prepare the sediment samples for analysis:

Freeze-Dryer: To desiccate wet sediment samples

Mortar and Pestle: To homogenize sample

Plastic Gloves: For handling polyvials prior to irradiation.

Sample Polyvials: Olympic Plastics 2/5 dram conventional polyethylene polyvials or equivalent.

Sample Transfer Spatula: To load dry sediment into polyvials.

Balance: Top loading with accuracy of 0.01 g.

Analytical Balance: With an accuracy of 0.0001 g.

Soldering Iron: To heat seal filled polyvials.

5.0 PROCEDURES

All sediment samples are freeze-dried and mechanically powdered with a mortar and pestle prior to loading.

5.1 Preparation of Samples

When samples are received frozen, they are thawed, and excess water is aspirated from the surface. The samples are mixed with a plastic spatula and subsampled into polyethylene vials. The original sample container is resealed and refrozen and the subsample is freeze dried and ground.

5.2 Sample Loading

Plastic gloves are generally worn while handling sample polyvials to avoid contamination. This precaution is especially important when analyzing sandy or carbonate sediments with lower trace element concentrations. Also, open polyvials are covered with lintless filter paper at all times until sample loading and cap closure.

5.2.1 Pre-cleaned polyvials are labelled with a permanent ink marker and tared to the nearest 0.1 mg using an analytical balance.

5.2.2 Approximately 0.50 g of dry powdered sediment is weighed to the nearest 0.01 g using an electronic top loading balance and placed in the appropriate labelled, pre-weighed polyvial sample container. Filled polyvials are weighed to the nearest 0.1 mg using an analytical balance and

the sample dry weight is determined by subtracting the empty, tare weight of the polyvial.

5.2.3 The hinge strap and cap tab are cut off each polyvial and the cap heat sealed using a soldering iron.

5.2.4 Samples are arranged in groups of 13 including 2 reference materials (comparator standards), 1 quality control sample, 8 samples (1 in duplicate) and 1 procedural blank.

5.2.5 Each group of samples is placed in an aluminum can provided by the TAMU Nuclear Science Center (NSC). Up to 6 aluminum cans (72 samples and 6 blanks) can be irradiated at one time by the NSC.

5.3 Sample Irradiation

Aluminum cans containing the sample polyvials are irradiated for 14 hours at the TAMU NSC TRIGA reactor using a continuously rotating, long-tube rotisserie device. The irradiation is conducted entirely by NSC staff personnel. The nominal thermal neutron flux for the irradiation is 1.0×10^{18} neutrons/cm^2. Irradiated samples are allowed to decay for 10 days and then released by the NSC for counting.

5.4 Sample Counting

Gamma-ray spectra are acquired for each sample using high resolution pure germanium detectors linked to Nuclear Data multi-channel analyzers used in the pulse height analysis mode.. Detector efficiencies are typically 20-25% with an observed resolution of 1.8-1.9 KEV full-width half-max at 1332.5 KEV. Analog to digital convertor (instrumental) dead time is kept at $\leq$ 10%.

5.5 Sample Calculation

Peak extraction and NAA calculations are accomplished using Nuclear Data proprietary PEAK and NAA programs running on a VAX GPX Workstation. These analytical determinations are made by direct comparison with comparator standards (standard reference materials) having known concentrations of Ba, Ce, Co, Cr, Fe, Hf, Rb, Sb, Sc and Th. Elemental concentrations in comparator standards have been previously determined during multiple irradiations using single element atomic absorption standards. The comparator standards are prepared, irradiated and analyzed at the same time and under the same conditions as the

sediment samples they are used to quantitate. Method detection limits for each element (MDL) are calculated based on the procedural blank.

6.0 QUALITY CONTROL

Quality control samples are processed in a manner identical to actual samples.

6.1 Procedural Blank

One procedural blank is run with every 12 sample aluminum can. Blank levels are generally below the MDL for all the elements of interest. For the infrequent case where there is a detectable blank for an element of interest, the concentration datum is reported with a blank correction.

6.2 Duplicate Samples

Depending on the sample mass available for analysis, one sample in every aluminum can group is run in duplicate. Control charts are kept of the average percent difference ((($|C1-C2|/C2)*100$) among duplicate determinations If the average percent difference exceeds 10%, analyses are halted and sample preparation techniques modified to return sample heterogeneity to ≤ 10%. All sample groups which exceeded the 10% limit are reanalyzed.

6.3 Reference Material

One sediment reference material, as closely matching the sample set as possible, is run with each aluminum can sample group (i.e. 13 polyvials). Expected concentrations of the elements of interest in reference materials are confirmed during multiple irradiations using single element atomic absorption standards. Control charts are maintained of the average percent deviation ((($|C_{obs}-C_{exp}|/C_{exp})*100$) among the reference material determinations. If the average percent deviation exceeds 10%, analyses are halted and sample preparation techniques modified to return sample heterogeneity to ≤ 10%. All sample groups which exceeded the 10% limit are reanalyzed.

7.0 REPORTING AND PERFORMANCE

7.1 Reporting Units

Reporting units for elements of interest are mg/kg (dry weight) except for Fe which is reported as % dry weight.

7.2 Minimum Method Performance Criteria

The minimum method performance standard is to have detectable levels of all elements of interest in 99% of the elemental determinations conducted.

7.3 Significant Figures

Results are reported to two significant figures for all elements except Fe, Sc and Th which are reported to three significant figures.

TOTAL ORGANIC AND CARBONATE CARBON CONTENT OF SEDIMENTS

1.0 INTRODUCTION

Precise measurements of total organic and carbonate carbon are necessary for interpreting trace organic contamination. Carbon concentrations are determined on freeze-dried (or oven-dried at 40° to 50°C) sediment using a LECO Model 523-300 induction furnace (or equivalent) to burn samples in an oxygen atmosphere. The carbon dioxide that is produced is swept out of the furnace's combustion chamber by the oxygen flow. The gases then pass through a dust trap and two reaction tubes. The first reaction tube is a two-stage chamber with the first stage consisting of manganese dioxide. The manganese dioxide absorbs the sulfur oxides that may have formed during combustion. The second stage is made of anhydrone which removes water vapor from the gas stream. The second tube, filled with platinized silica, is maintained at an elevated temperature by an external heating case. The contents of this tube act as a catalyst to convert any carbon monoxide present into carbon dioxide. Carbon dioxide is detected and quantified with a Horiba PIR-2000 infrared detector. The output signal from the Horiba is sent to a HP 3396A integrator which reports the quantity of carbon dioxide as a peak area.

Total organic carbon is determined after sample acidification. Carbonate carbon is determined as the difference between total carbon and total organic carbon.

2.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

2.1 Sample Collection

Sediments are collected in precleaned and/or pre-combusted (400°C) glass jars, or core liners and frozen (-20°C) in the field.

2.2 Sample Preservation and Storage

Sediment samples are shipped frozen to the laboratory and stored at -20°C until analysis. After subsampling excess sample is archived at -20°C in the dark.

3.0 APPARATUS AND MATERIALS

3.1 Labware and Apparatus

The following labware and equipment is needed to perform the total organic carbon and total carbon analyses:

Freeze Drier: Capable of freeze drying sediment at -40°C.

Mortar and Pestal: 500-mL mortar or other suitable container.

LECO Model 523-300 Induction Furnace

Horiba PIR-2000 Infrared Detector: Or other suitable detector.

HP 3396A Integrator: Or other suitable recorder/integrator.

Glass Measuring Scoop

Drying Oven: Capable of maintaining 40° to 50°C.

Analytical Balance: Capable of weighing to 1 mg.

Rotameter: Part No. 112-02, Cole-Parmer, Inc.

Flow Controller: Part No. 42300513, Veriflo Corp.

Note: Volumetric glassware for accelerator measurement and analytical balances must be calibrated.

3.2 Reagents

The following reagents are required:

10% HCl in Methanol (V:V)

LECO Iron Chip Accelerator: Part No. 501-077, Leco Corp.

LECO Copper Metal Accelerator: Part No. 501-263, Leco Corp.

LECO Combustion Crucibles: Part No. 528-018, Leco Corp.

LECO Pin and Ring Carbon Standards: Range: 0.1 to 1.0% carbon.

4.0 PROCEDURE

4.1 Leco System Preparation

The first step in operating the LECO furnace is to turn it on by flipping all switches on the front panel to the "ON" (up) position. The "Grid Tap Switch" should be set to the "MED" position. The instrument then needs a warm-up period of at least 30 minutes. When the furnace has had time to warm-up, close the oven on the right side of the instrument (pedestal up) and open the valve on the oxygen tank; set the regulator pressure to 40 psi. Open the toggle valve and allow oxygen to flow through the system for 15 seconds and then check the flow rate using the rotameter. Set to the 150 mark on the rotameter tube with the knob on the flow controller to the right of the rotameter. After 30 seconds of correct flow, zero the panel meter on the front of the Horiba Infrared Analyzer. Set the Horiba Infrared Analyzer detector range to 3, and the span to 0.

4.2 Total Carbon Determination

4.2.1 Sample Preparation

Weigh 100 to 500 mg (to the nearest milligram) of freeze dried (or oven dried), finely ground, homogenized sediment into a tared, carbon-free combustion crucible. The amount of sample depends upon the expected carbon concentration. Ideally between 0.5 mg and 8.6 mg of carbon should be combusted to fall within the range of the standard curve.

Add one scoop each of the copper and iron chip accelerators to all the weighed crucibles containing samples. All crucibles should be kept covered with aluminum foil prior to analyses.

4.2.2 Sample Analyses

Place the crucible on the oven pedestal. Close the oven and start the oxygen flow. Allow the oxygen to flow for 15 seconds and then check the flow rate on the rotameter and adjust the flow, if needed. After 15 seconds of correct flow, push the pedestal lever in to start the induction furnace. At the same time push the "START" button on the HP integrator. About 20 seconds after the furnace is activated the metals should begin to burn. After about another 20 seconds the detector should begin to register carbon

dioxide in the gas flow and the integrator should begin to show a peak. At this point carefully pull the lever out to turn the furnace OFF -- be sure that you don't open the combustion chamber. Once the integrator has returned to baseline, carefully open the oven and press STOP on the integrator. Use a pair of large tweezers or tongs to take the hot crucible off the oven pedestal and place it on a non-flammable heat-resistant surface to cool. Repeat this procedure for all crucibles to be run.

4.2.3 Standard Analyses

Standard Leco pin and ring carbon standards are placed into an empty crucible with one scoop of the copper accelerator. Standards are analyzed per the identical procedure as outlined in Section 4.2.2.

4.3 Total Organic Carbon Determination

4.3.1 Sample Preparation

Weigh an appropriate amount of freeze dried (or oven dried) sample as per step 4.2.1 into a tared crucible. Add small amounts of 10% HCl in methanol solution slowly to the sample until all bubbling stops. Use a minimal amount of acid. Dry the treated samples overnight at 50°C in the drying oven.

4.3.2 Sample Analyses

Combust and analyze as indicated in Section 4.2.2.

4.3.3 Standard Analyses

Standards are analyzed per the identical procedure as outlined in Section 4.2.3.

4.4 Total Carbonate Carbon Content

Carbonate content is determined by subtracting the total organic carbon concentration from the total carbon concentration. To express as percent calcium carbonate, instead of total carbonate carbon content, multiply this result by 8.33.

5.0 STANDARDIZATION AND CALCULATIONS

Prior to combusting samples, a set of standards is run to determine a standard curve. Standard curves vary slightly from day to day.

5.1 To determine the curve, combust a set of five standards at varying concentrations. Several standard rings and/or pins may need to be run initially to bring the system to correct operating conditions; the data collected will be discarded. The values of the standards in the set should be selected to cover the 0.1 to 1.0% carbon range (1 gram basis).

5.2 A graphics package on a Macintosh (such as KaleidaGraph) is used to make a graph of carbon percentage vs. integrator counts. This software is used to determine a best fit equation for the data. R should be no less than .99 or the data set should be discarded and another set of five calibration points should be run and plotted. This equation will be used to determine the carbon percentage of samples for that day.

5.3 The counts reported by the integrator for a sample are simply entered for X in the equation and Y becomes an intermediate value. The Y value is divided by the sample weight in grams to determine the percent carbon.

6.0 QUALITY CONTROL

Quality control samples are processed in an identical manner as the actual samples.

6.1 A method blank is run with every 20 samples, or with every sample set, whichever is more frequent. Blank levels should be no more than 3x method detection limit (MDL).

6.2 Duplicate samples are run every 20 samples, or with every sample set. Duplicates should be ± 20% for low level (<1.0% carbon) samples and ± 10% for normal/high level (>1.0% carbon) sample. Duplicates may be somewhat less precise for very inhomogeneous samples (i.e., peats, samples containing twigs, grasses, etc.).

6.3 Reference Materials: Leco pin and ring carbon standards are run as reference materials and standards.

7.0 REPORTING AND PERFORMANCE CRITERIA

7.1 Reporting Units

Reporting units are percent organic carbon (on a dry weight basis) and percent carbonate carbon (on a dry weight basis). All data will be reported using the Data Reporting Form.

7.2 Minimum Method Performance Criteria

The minimum method performance standard for the method is detection of 0.02 percent carbon in a sample.

7.3 Significant Figures

Results are reported to two (2) significant figures.

7.4 Duplicate Analyses

All duplicate analyses are reported. Duplicate analyses are run at least every 20 samples.

7.5 Reference Materials

Leco pin and ring carbon standards are analyzed as reference materials and standards.

8.0 EXAMPLE FORMS

8.1 Organic Carbon Analysis Form

8.2 TOC/TIC Data Reporting Form

SEDIMENT GRAIN SIZE ANALYSES - GRAVEL, SAND, SILT AND CLAY ONLY

1.0 INTRODUCTION

Sediment texture is an important variable in the evaluation of contaminant concentrations and benthic systems. Numerous studies have shown a correlation between contaminant concentration and grain size. In benthic ecosystem studies, cross correlations between stations are often dependent upon substrate characteristics.

The most common method for the analysis of silt and clay sized particles is the pipette method (Folk, 1974). It is based on the settling velocity of the particles, usually computed on the basis of Stokes' Law. At given times, small volumes of suspension are withdrawn, evaporated, and the residue weighed.

2.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

2.1 Sample Collection

Sediment can be collected in glass jars, core liners or plastic bags by appropriate sampling techniques (i.e., scoop, grab or box core). The preferred storage medium is plastic bags. At a minimum, 50 g of sample is placed in a separate plastic Ziplock or Whirl-Pak bag, sealed and labeled.

2.2 Sample Preservation and Storage

Samples should be refrigerated. It is recommended that samples **not** be frozen.

3.0 APPARATUS AND MATERIALS

3.1 Labware and Apparatus

The following labware and equipment is needed to perform the grain size analyses:

Large Mason jars: 1 pint.

Beakers: 50 mL.

Graduated Cylinders: 1-liter.

Analytical Balance: 0.1 mg accuracy.

Pipette: 20-mL capacity.

Drying Ovens: Maintained at 40°-50°C and 100°-130°C.

Timer: 1 second intervals.

Shaker Table

Note: Volumetric glassware and analytical balances must be calibrated.

3.2 Reagents

The following reagents are required:

Sodium Hexametaphosphate Solution: Concentration: 5.5 g/L.

Distilled Water

4.0 PROCEDURE

4.1 Preparation of Samples for Dry-Sieving and Pipette Analysis

Homogenize sample (massage sample bag by hand) and place ~15-20 grams of sample in a large, glass jar. This sample size is chosen to minimize the interference of grains with each other during settling and the possibility of flocculation; as well as to maximize the amount of material to be weighed (i.e., with small samples the error in weighing becomes large with respect to the sample weight). The sample is treated with ~50-100 mL of 30% hydrogen peroxide (volume varies with amount of organic matter present) for 12 hours prior to analyses to oxidize organic matter. The sample is washed with distilled water to remove soluble salts. Four hundred (400) mL of sodium hexametaphosphate solution (~5.5 g/L) is added to disperse the sample, followed by shaking for ~24 hours on shaker table.

4.2. Size Analysis of Sand/Gravel Fraction By Dry-Sieving

At this point all size fractions are in the jar. A 62.5 micron screen is placed over a 1-liter graduated cylinder. The sample containing the dispersed sediment is poured over the screen and washed with dispersant

to rinse any remaining fine-grained sediment into the cylinder. This separates the gravel/sand fraction (on the screen) from the silt/clay fraction (in the cylinder). The coarse fraction is washed into a preweighed beaker with distilled water and placed in an oven (100°-130°C) to dry for 24 hours. The beaker is removed from the oven and left to cool to room temperature. The beaker is left open in the room where weighing is to take place for several hours to allow equilibration with the moisture content of the atmosphere. The beaker is weighed to 0.1 mg with an analytical balance. If both sand and gravel are required, the sand fraction is dry sieved at 2 mm (-1.0 phi) and 62.5 micron (4 phi) intervals to separate gravel from sand-sized material. The weights of the gravel (>2 mm) and sand-sized (62.5 micron to 2 mm) material are recorded on data sheets.

4.3 Silt/Clay Sized Material by Settling

The graduated cylinder containing the silt/clay material is filled to exactly one liter volume with dispersant solution. The cylinder is stirred vigorously and left to stand for one (l) day. If the cylinder shows no sign of flocculation, analyses may proceed. If it starts flocculating, the sample will have to be discarded and the procedure restarted.

4.3.1 The fine fraction is analyzed at 4 phi and 8 phi intervals. Two labelled beakers are preweighed to 0.1 mg.

4.3.2 The cylinder is stirred vigorously starting at the bottom and working up until all the sediment is distributed uniformly throughout the cylinder. At the end of the vigorous stirring, long, smooth strokes the full length of the cylinder (from the bottom until the stirring rod breaks the surface) are used. THE NEXT STEP IS EXTREMELY IMPORTANT!!! As soon as the rod emerges for the last time, start the timer. Insert the pipette to a depth of 20 cm, and at the end of 20 seconds, withdraw exactly 20 mL (this is the 4 phi aliquot). This is the most important single step, because on it the subsequent analysis is based (the dry weight of the 4 phi aliquot is the total weight of the silt + clay fraction). Pipette the suspension into a preweighed beaker, rinse the pipette with 20 mL of distilled water, and add the rinse water to the same beaker.

4.3.3 At the 2:03:00 (two hours, 3 minutes) time, withdraw a 20 mL aliquot at a depth of 10 cm; this is the 8 phi

aliquot. Pipette the suspension into a different preweighed beaker, rinse with 20 mL of distilled water and add to the beaker.

4.3.4 The beakers are placed in an oven and evaporate to dryness for at least 24 hours at 100-130°C. After 24 hours, they are removed from the oven and left to cool to room temperature. They are left open in the room where weighing is to take place for several hours, so that they can come to equilibrium with the moisture content of the atmosphere. The beakers are weighed to 0.1 mg with an analytical balance, and the weights recorded on a data sheet.

5.0 CALCULATIONS

5.1 The 4 and 8 phi dry weights include the weight of the added dispersant. Multiply the dispersant weight (g/L) by the fraction of the total solution removed (20/1000) and subtract from the aliquot weight. This total is then multiplied by 50 (1000 mL/20 mL) to yield the sample weight of the silt + clay fraction.

Total dry sample weight: Three weights are needed to calculate the total dry sample weight.

wt. sand (2 mm to 62.5 micron size range)

+ wt. gravel (2 mm and greater size range)

+ wt. of 4 phi residue

= total dry sample weight

% gravel = wt. gravel fraction / total dry sample wt.

% sand = wt. sand fraction / total dry sample wt.

% silt = [(wt. 8 phi residue - dispersant) x 50] / total dry sample wt.

% clay = {[(wt. 4 phi-wt. 8 phi) - dispersant] x 50} / total dry sample wt.

6.0 QUALITY CONTROL

Duplicate samples are run every 20 samples.

7.0 REPORTING AND PERFORMANCE CRITERIA

7.1 Reporting Units

Reporting units are percent gravel, sand, silt and clay on a weight basis.

7.2 Minimum Method Performance Criteria

The minimum method performance standard for the method is detection of 0.5 percent of each fraction.

7.3 Significant Figures

Results are reported to three (3) significant figures.

7.4 Duplicate Analyses

All duplicate analyses are reported. Duplicate analyses are run at least every 20 samples.

8.0 REFERENCES

Folk, Robert L., 1974. Petrology of Sedimentary Rocks. Hemphill Publishing Company, Austin, Texas. 182 pp.