AlliedSignal Canada Inc.

Clark Island Site

Grande-Ile Shoreline Sediments Characterization

Sediments Toxicity

July 1993

TECSULT

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1.0 OBJECTIVES

The objectives of the February-March 1993 sediment characterization efforts were presented in the main report. These included the delineation of the contaminated area, an update of the risk values and the development of a more complete data-base. The bulk of the work was based on the interim sediment quality guidelines recently issued by MENVIQ.

It was considered appropriate to develop a preliminary appreciation of whether the river bottom sediments from the Grande-Ile shoreline present any ecotoxicity. This was achieved using the new concept of AVS (Acid Volatile Sulfides). According to this concept, AVS would control metals availability to the aquatic environment and hence would determine the ecotoxicity of the sediment.

The results of this preliminary toxicity assessment are presented separately since the AVS toxicity screening approach is relatively new to the regulatory community.

2.0 FIELD WORK

The field work for the preliminary sediments toxicity assessment along Grande-Ile shoreline was carried out at the same time as for the sediments chemical characterization, from February 22 to March 4, 1993. The total number of sampling stations was thirty-nine (39). Most of the stations (34) were located along Grande-Ile shoreline. Five (5) additional stations were located along the North-West shoreline of Clark Island. The location of the sampling stations is shown on Figure 2.1 (see in Appendix B). The sampling points are identified SE-93-01 to SE-93-85.

As for the sediments chemical characterization, all the samples were obtained from the surface by using the TECSULT sampler. Since the analytical tests required that the sample should not be exposed to ambient air, this type of sampler was best suited for this purpose. Each glass jar was filled with water to avoid air space on top of the sediment. A polyethylene liner was also inserted under the cover. Photographies of field work are presented in Appendix A.

The pertinent data for all collected samples during the field work as well as visual description of all the samples are presented in the main report.

3.0 AVS AND SEM THEORY

The AVS methodology was developed by Ditoro D. et al. in 1990, in order to estimate the sediments toxicity. It is widely accepted that the total metal concentrations in sediments is not an appropriate measure of the "free" and bioavailable fraction of the total chemical present. To develop toxicity estimates based on chemical measurements, one needs to estimate the bioavailable fraction of the total metals present. It is argued that sediment Sulfides control metal bioavailability. Sulfides are common in many freshwater and marine sediments and are the predominant form of Sulphur in anaerobic sediments. The ability of Sulfides to react with metal ions in order to form water insoluble precipitates forms the basis of the AVS theory.

It has been shown that the solid-phase sediment Sulfides that are soluble in cold acid, termed acid volatile Sulfides (AVS), are a key factor for controlling the toxicity of several heavy metals. According to Ditoro D. et al., no toxicity is observed from heavy metals when bound to sediment and when, on a molar basis, the concentration of AVS is greater than the sum of the molar concentrations of the Simultaneously Extracted Metals (SEM). When the ratio of

the metals concentration to AVS (∑SEM/AVS) exceeds 1.0, toxicity potentially appears.

4.0 SAMPLING AND TESTING

At thirty-nine (39) stations, a sample was collected directly in a jar, for the Acid Volatile Sulfides (AVS) and Simultaneously Extracted Metals (SEM) analyses. The samples were placed in an icebox and brought to the analytical laboratory the same day.

The AVS and SEM contents were measured on the thirty-nine (39) samples collected. These analyses were realized at the laboratory of McGill University. Ten (10) duplicate samples were submitted to the National Scientific Research Institute (INRS) in Quebec City. The analytical methods and the detection limits of these analyses are presented in Table 4.1. The EPA draft analytical method is presented in Appendix C.

5.0 SEDIMENTS TOXICITY

5.1 Acid Volatile Sulfides (AVS) and Simultaneously Extracted Metals (SEM) contents

As mentioned previously, thirty-nine (39) samples were tested to determine the AVS and SEM concentrations on a molar basis. The analytical test results are presented in Table 5.1.

AVS represents the Sulfides concentration and SEM represents the concentration of metals binds to the Sulfides. In Table 5.1, the AVS are compiled as well as the SEM concentrations for the four (4) selected metals (Cd, Cu, Hg, Zn), together with the SEM summation for these four (4) metals. Also, in this table,

TABLE 4.1
ALLIED–SIGNAL INC – CLARK ISLAND SITE
GRANDE–ILE SHORELINE SEDIMENTS CHARACTERIZATION
ANALYTICAL METHODS AND DETECTION LIMITS
AVS AND SEM CONTENTS

PARAMETER	METHOD (1)	DETECTION LIMIT
AVS	EPA	0.05 μmole/g
SEM [Cd]	EPA	0.0001 mg/l
SEM [Cu]	EPA	0.001 mg/l
SEM [Hg]	EPA	0.0001 mg/l
SEM [Zn]	EPA	0.002 mg/l

NOTE (1) EPA: Environmental Protection Agency : draft analytical method for determination of acid volatile sulfides and simultaneously extracted metals in sediment – August 1991 (see appendix C).

TABLE 5.1
ALLIED–SIGNAL INC – CLARK ISLAND SITE
GRANDE–ILE SHORELINE SEDIMENTS CHARACTERIZATION
SEDIMENTS TOXICITY RESULTS

SAMPLE NUMBER	WATER DEPTH (m)	RIVER BOTTOM ELEVATION (m)	SIMULTANEOUSLY EXTRACTED METALS (umole/g)					ACID (2) VOLATILE SULFIDES (umole/g)	ΣSEM/AVS (--)
			SEM[Cd]	SEM[Cu]	SEM[Hg]	SEM[Zn]	ΣSEM (1)		
SE–93–01	1.30	45.20	0.395	2.050	<0.0001	162.50	164.95	251.00	0.66
SE–93–02	1.60	44.90	0.420	1.900	<0.0001	192.00	194.32	168.00	1.16
SE–93–05	1.35	45.15	0.270	3.400	<0.0001	132.50	136.17	126.00	1.08
SE–93–08	1.30	45.20	0.120	3.730	<0.0001	46.00	49.85	27.00	1.85
SE–93–09	1.65	44.85	0.350	1.400	<0.0001	189.00	190.75	164.00	1.16
SE–93–12	1.60	44.90	0.120	1.800	<0.0001	98.00	99.92	127.00	0.79
SE–93–16	1.10	45.40	0.013	0.100	<0.0001	4.95	5.06	0.94	5.39
SE–93–19	1.20	45.30	0.007	0.110	<0.0001	3.40	3.52	3.60	0.98
SE–93–20	1.70	44.80	0.100	1.490	<0.0001	30.00	31.59	8.30	3.81
SE–93–23	1.30	45.20	0.020	0.298	<0.0001	10.00	10.32	5.60	1.84
SE–93–24	1.50	45.00	0.017	0.209	<0.0001	7.20	7.43	1.90	3.91
SE–93–26	1.20	45.30	0.015	0.157	<0.0001	12.50	12.67	1.80	7.04
SE–93–27	1.40	45.10	0.027	0.482	<0.0001	56.00	56.51	11.40	4.96
SE–93–30	1.10	45.40	0.006	0.082	<0.0001	4.40	4.49	1.90	2.36
SE–93–31	1.50	45.00	0.020	0.662	<0.0001	71.00	71.68	5.30	13.52
SE–93–33	1.25	45.25	0.014	0.337	<0.0001	24.00	24.35	4.40	5.53

(1) : For the SEM calculation, a value representing half the detection limit was used when the concentration was not detected

(2) : For the non detected value, a value representing half the detection limit was used in the calculation

TABLE 5.1 (CONTINUED)
ALLIED–SIGNAL INC – CLARK ISLAND SITE
GRANDE–ILE SHORELINE SEDIMENTS CHARACTERIZATION
SEDIMENTS TOXICITY RESULTS

SAMPLE NUMBER	WATER DEPTH (m)	RIVER BOTTOM ELEVATION (m)	SIMULTANEOUSLY EXTRACTED METALS (umole/g)					ACID (2) VOLATILE SULFIDES (umole/g)	Σ SEM/AVS (--)
			SEM[Cd]	SEM[Cu]	SEM[Hg]	SEM[Zn]	Σ SEM (1)		
SE–93–34	1.55	44.95	0.015	0.468	<0.0001	40.00	40.48	6.30	6.43
SE–93–37	1.20	45.30	0.001	0.076	<0.0001	5.50	5.58	2.80	1.99
SE–93–38	1.45	45.05	0.030	0.450	<0.0001	55.00	55.48	9.20	6.03
SE–93–40	1.20	45.30	0.007	0.111	<0.0001	2.50	2.62	<0.2	26.18
SE–93–41	1.50	45.00	0.016	0.359	<0.0001	32.00	32.38	6.40	5.06
SE–93–44	1.50	45.00	0.005	0.297	<0.0001	2.40	2.70	0.47	5.75
SE–93–45	1.70	44.80	0.018	0.320	<0.0001	24.50	24.84	6.50	3.82
SE–93–48	1.15	45.35	0.007	0.035	<0.0001	1.90	1.94	2.80	0.69
SE–93–49	1.65	44.85	0.006	0.049	<0.0001	1.10	1.16	0.47	2.46
SE–93–52	1.25	45.25	0.013	0.028	<0.0001	2.40	2.44	1.40	1.74
SE–93–53	1.70	44.80	0.006	0.032	<0.0001	0.29	0.32	<0.2	3.23
SE–93–58	1.20	45.30	0.017	0.030	<0.0001	3.15	3.20	3.00	1.07
SE–93–61	1.20	45.30	0.017	0.064	<0.0001	2.40	2.48	1.80	1.38
SE–93–62	1.75	44.75	0.014	0.158	<0.0001	9.90	10.07	7.30	1.38
SE–93–69	1.55	44.95	0.021	0.157	<0.0001	3.65	3.83	2.10	1.82
SE–93–75	1.85	44.65	0.012	0.059	<0.0001	1.60	1.67	3.60	0.46
SE–93–75A	1.80	44.70	0.052	0.145	<0.0001	10.00	10.20	13.60	0.75

(1) : For the SEM calculation, a value representing half the detection limit was used when the concentration was not detected

(2) : For the non detected value, a value representing half the detection limit was used in the calculation

TABLE 5.1 (CONTINUED)
ALLIED–SIGNAL INC – CLARK ISLAND SITE
GRANDE–ILE SHORELINE SEDIMENTS CHARACTERIZATION
SEDIMENTS TOXICITY RESULTS

SAMPLE NUMBER	WATER DEPTH (m)	RIVER BOTTOM ELEVATION (m)	SIMULTANEOUSLY EXTRACTED METALS (umole/g)					ACID (2) VOLATILE SULFIDES (umole/g)	ΣSEM/AVS (–)
			SEM[Cd]	SEM[Cu]	SEM[Hg]	SEM[Zn]	ΣSEM (1)		
SE–93–75B	1.50	45.00	0.006	0.054	<0.0001	1.30	1.36	0.69	1.97
SE–93–81	0.65	45.85	0.098	1.650	<0.0001	13.00	14.75	2.90	5.09
SE–93–82	0.75	45.75	0.034	1.340	<0.0001	12.00	13.37	5.90	2.27
SE–93–83	0.85	45.65	0.044	1.810	<0.0001	7.00	8.85	1.20	7.38
SE–93–84	0.60	45.90	0.009	2.120	<0.0001	3.00	5.13	<0.2	51.29
SE–93–85	0.70	45.80	0.019	1.465	<0.0001	16.50	17.98	16.20	1.11

(1) : For the SEM calculation, a value representing half the detection limit was used when the concentration was not detected

(2) : For the non detected value, a value representing half the detection limit was used in the calculation

the (∑SEM/AVS) ratio is calculated to indicate sediments toxicity. As previously mentioned, when the ratio (∑SEM/AVS) exceeds 1.0, toxicity potentially appears.

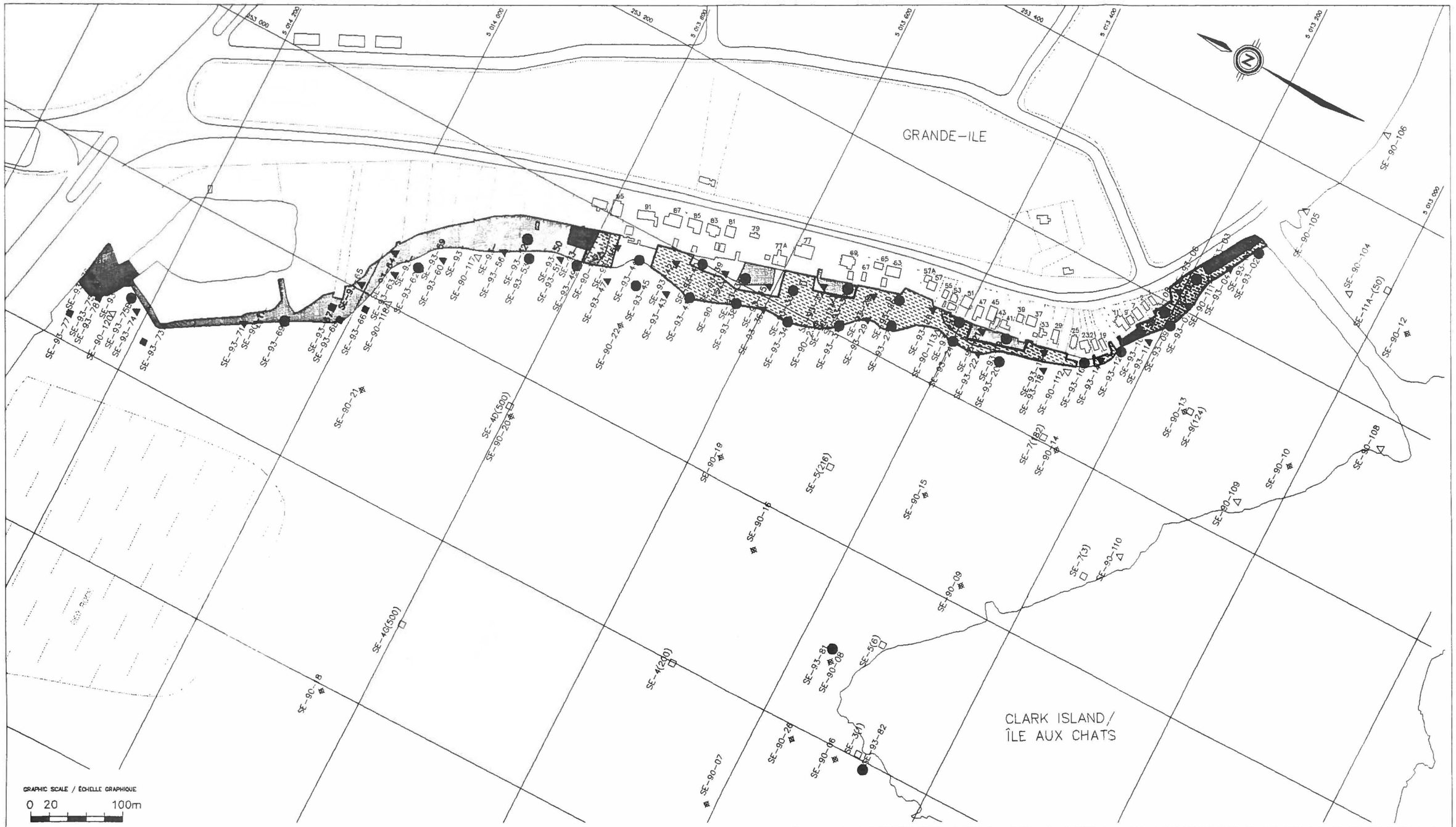
According to the test results, it appears that the majority of the sediment samples may be toxic for benthic organisms. In fact, the ratio (∑SEM/AVS) exceeds 1.0 for 85% of the collected samples in Priority Zone II. The ratio values vary from 0.5 to 27 in this zone. Zones of various potential toxicity are illustrated for Priority Zone II in Figure 5.1.

From stations SE-93-01 to SE-93-23, the ratio (∑SEM/AVS) is generally in the range of 1.0 to 3.0 and sometimes below 1.0. Sediments in this area would not be considered very toxic. However, total Zinc concentrations in this zone are very high. This situation is explained by the fact that the sediments are very fine, and consequently contain high levels of Sulfides. When the Sulfides (AVS) content is important, the toxicity values (∑SEM/AVS) decrease because heavy metals are bound to Sulfides.

From stations SE-93-23 to SE-93-46, the ratio (∑SEM/AVS) is typically greater than 3. Sediments in this zone would be characterized by toxicity. This situation results from the predominance of coarser sediments and the significant presence of heavy metals. In coarse sediments, Sulfides (AVS) are typically lower and the bioavailability of metals in sediments is potentially more important.

For the area located downstream of station SE-93-46, the ratio ∑SEM/AVS is in the range of 1.0 to 3.0. Considering that total metal concentrations in this zone are below the new Quebec guidelines, additional characterization work is not considered appropriate.

In Priority Zone I, all collected samples have a ratio (∑SEM/AVS) above 1.0. The ratio values vary from 1.15 to 58.0.



Allied Signal
ENGINEERED MATERIALS

PRELIMINARY TOXICITY ASSESSMENT AREAL EXTENT ZONES

N° contrat/contract	Échelle / Scale	Date
4361-1000	1:4000	APRIL 1993

FIGURE : 5.1

0696 0493

5.2 Quality Assurance and Quality Control Program

An internal QA/QC program was implemented at the McGill laboratory where nine (9) samples were tested in duplicate. The results, as shown on Table 5.2, indicate that the duplicate samples have concentration values in the same range.

The external QA/QC program was realized on ten (10) samples by INRS. It should be noted that the samples were collected at the same station but are not split samples. During the field work, it was not possible to collect large volumes of sediment material and to separate these into two split-samples. The reason is that the toxicity test requires that the sample should not be in contact with ambient air. In order to fulfil this requirement, two different samples were collected at the same locations and were considered as duplicate.

The results of this external QA/QC program are compiled on Table 5.3. The measured metals and AVS concentration values are in the same range of values. For both laboratories, Zinc is the most important contaminant. With respect to the ratio ($\sum$SEM/AVS) obtained from both laboratories, the same conclusion can be drawn, i.e. sediments in most stations exhibit potential aquatic toxicity.

In conclusion, considering that the AVS and SEM methodology from EPA is actually a draft method that is not used by the laboratories on a day-to-day basis, and that the duplicate samples sent to the two laboratories are not split samples obtained from the same large sample, the results are considered acceptable.

TABLE 5.2
ALLIED–SIGNAL INC – CLARK ISLAND SITE
GRANDE–ILE SHORELINE SEDIMENTS CHARACTERIZATION
RESULTS OF THE INTERNAL QA/QC PROGRAM FROM MC GILL UNIVERSITY

SAMPLE NUMBER	TEST NUMBER	SIMULTANEOUSLY EXTRACTED METALS (umole/g)					ACID (2) VOLATILE SULFIDES (umole/g)	ΣSEM/AVS (--)
		SEM[Cd]	SEM[Cu]	SEM[Hg]	SEM[Zn]	Σ SEM (1)		
SE–93–01	01	0.370	1.800	<0.0001	154.00	156.17	248.00	0.63
	02	0.420	2.300	<0.0001	171.00	173.72	254.00	0.68
	AVER.	0.395	2.050	<0.0001	162.50	164.95	251.00	0.66
SE–93–05	01	0.290	3.200	<0.0001	132.00	135.49	136.00	1.00
	02	0.250	3.600	<0.0001	133.00	136.85	116.00	1.18
	AVER.	0.270	3.400	<0.0001	132.50	136.17	126.00	1.09
SE–93–16	01	0.013	0.104	<0.0001	5.10	5.22	0.94	5.55
	02	0.012	0.095	<0.0001	4.80	4.91	0.94	5.22
	AVER.	0.013	0.100	<0.0001	4.95	5.06	0.94	5.39
SE–93–26	01	0.014	0.171	<0.0001	12.00	12.19	1.90	6.41
	02	0.015	0.142	<0.0001	13.00	13.16	1.70	7.74
	AVER.	0.015	0.157	<0.0001	12.50	12.67	1.80	7.08
SE–93–40	01	0.007	0.123	<0.0001	2.60	2.73	<0.2	27.30
	02	0.007	0.099	<0.0001	2.40	2.51	<0.2	25.06
	AVER.	0.007	0.111	<0.0001	2.50	2.62	<0.2	26.18
SE–93–45	01	0.015	0.314	<0.0001	25.00	25.33	6.40	3.96
	02	0.020	0.325	<0.0001	24.00	24.35	6.60	3.69
	AVER.	0.018	0.320	<0.0001	24.50	24.84	6.50	3.82
SE–93–58	01	0.016	0.029	<0.0001	3.20	3.25	3.10	1.05
	02	0.018	0.031	<0.0001	3.10	3.15	2.90	1.09
	AVER.	0.017	0.030	<0.0001	3.15	3.20	3.00	1.07
SE–93–69	01	0.022	0.155	<0.0001	3.90	4.08	2.00	2.04
	02	0.020	0.158	<0.0001	3.40	3.58	2.20	1.63
	AVER.	0.021	0.157	<0.0001	3.65	3.83	2.10	1.83
SE–93–85	01	0.020	1.440	<0.0001	17.00	18.46	16.50	1.12
	02	0.018	1.490	<0.0001	16.00	17.51	15.90	1.10
	AVER.	0.019	1.465	<0.0001	16.50	17.98	16.20	1.11

(1) : For the SEM calculation, a value representing half the detection limit was used when the concentration was not detected
(2) : For the non detected value, a value representing half the detection limit was used in the calculation

TABLE 5.3
ALLIED–SIGNAL INC. – CLARK ISLAND SITE
GRANDE–ILE SHORELINE SEDIMENTS CHARACTERIZATION
RESULTS OF THE EXTERNAL QA/QC PROGRAM
MC GILL UNIVERSITY AND INRS INSTITUTE

SAMPLE NUMBER	SIMULTANEOUSLY EXTRACTED METALS (umoles/g)										ACID VOLATILE (2) SULFIDES (umole/g)		Σ SEM/AVS (-)	
	SEM [Cd]		SEM [Cu]		SEM [Hg]		SEM [Zn]		Σ SEM (1)					
	MCGILL	INRS	MCGILL	INRS	MCGILL	INRS	MCGILL	INRS	MCGILL	INRS	MCGILL	INRS	MCGILL	INRS
SE–93–02	0.420	0.120	1.900	3.470	<0.0001	<0.0001	192.00	47.30	194.32	50.89	168.00	46.20	1.16	1.10
SE–93–05	0.270	0.240	3.400	3.420	<0.0001	<0.0001	132.50	94.70	136.17	98.36	126.00	54.30	1.08	1.81
SE–93–09	0.350	0.240	1.400	6.400	<0.0001	<0.0001	189.00	102.50	190.75	109.14	164.00	103.50	1.16	1.05
SE–93–61	0.017	0.010	0.064	0.066	<0.0001	<0.0001	2.40	2.38	2.48	2.46	1.80	2.04	1.38	1.20
SE–93–62	0.014	0.014	0.158	0.122	<0.0001	<0.0001	9.90	5.18	10.07	5.32	7.30	0.72	1.38	7.38
SE–93–75	0.012	0.004	0.059	0.095	<0.0001	<0.0001	1.60	2.33	1.67	2.43	3.60	6.73	0.46	0.36
SE–93–75A	0.052	0.016	0.145	0.158	<0.0001	<0.0001	10.00	3.37	10.20	3.55	13.60	1.98	0.75	1.79
SE–93–75B	0.006	0.036	0.054	0.159	<0.0001	<0.0001	1.30	6.83	1.36	7.03	0.69	4.05	1.97	1.74
SE–93–81	0.098	0.029	1.650	2.310	<0.0001	0.0002	13.00	11.10	14.75	13.44	2.90	0.16	5.09	84.00
SE–93–83	0.044	0.006	1.810	2.250	<0.0001	<0.0001	7.00	2.33	8.85	4.59	1.20	2.14	7.38	2.14

(1) : For the SEM calculation, a value representing half the detection limit was used when the concentration was not detected
(2) : For the non detected value, a value representing half the detection limit was used in the calculation

5.3 Correlation Between Acid Volatile Sulfides and Grain Size

The correlation between the Acid Volatile Sulfides and the sediments grain size (presented in 1993 Grande-Ile Shoreline Sediments Characterization report) was analyzed in order to identify whether there is a relation between the two sediments characteristics. The correlation is illustrated on the semi log plot of Figure 5.2.

Based on this, it can be observed that Acid Volatile Sulfides values are higher when the percentage of fine particles in the sediment materials increases. This finding explains the decrease of sediments toxicity for fine sediments, and supports the idea that metals bioavailability in fine sediments is lower than in coarse sediments.

5.4 Correlation Between Total Metal Concentrations and Simultaneously Extracted Metals in Sediment

The correlations between the total metal concentrations and the simultaneously extracted metals were analyzed in order to verify if the analytical methods used by the two laboratories result in concentration values in the same range.

The correlations for Cadmium, Copper and Zinc are illustrated on Figures 5.3, 5.4 and 5.5 respectively. There is no correlation between the two analytical methods for Mercury since the simultaneously extracted Mercury was never detected.

Based on the Cadmium, Copper and Zinc correlations, it is noted that the concentrations obtained by the two analytical methods are in the same range. For each analytical method, it appears that Zinc is the most important contaminant.

ALLIED–SIGNAL INC. – CLARK ISLAND SITE
GRANDE–ILE SEDIMENT CHARACTERIZATION
CORRELATION BETWEEN SEDIMENTS GRAIN–SIZE AND ACID VOLATILE SULFIDES

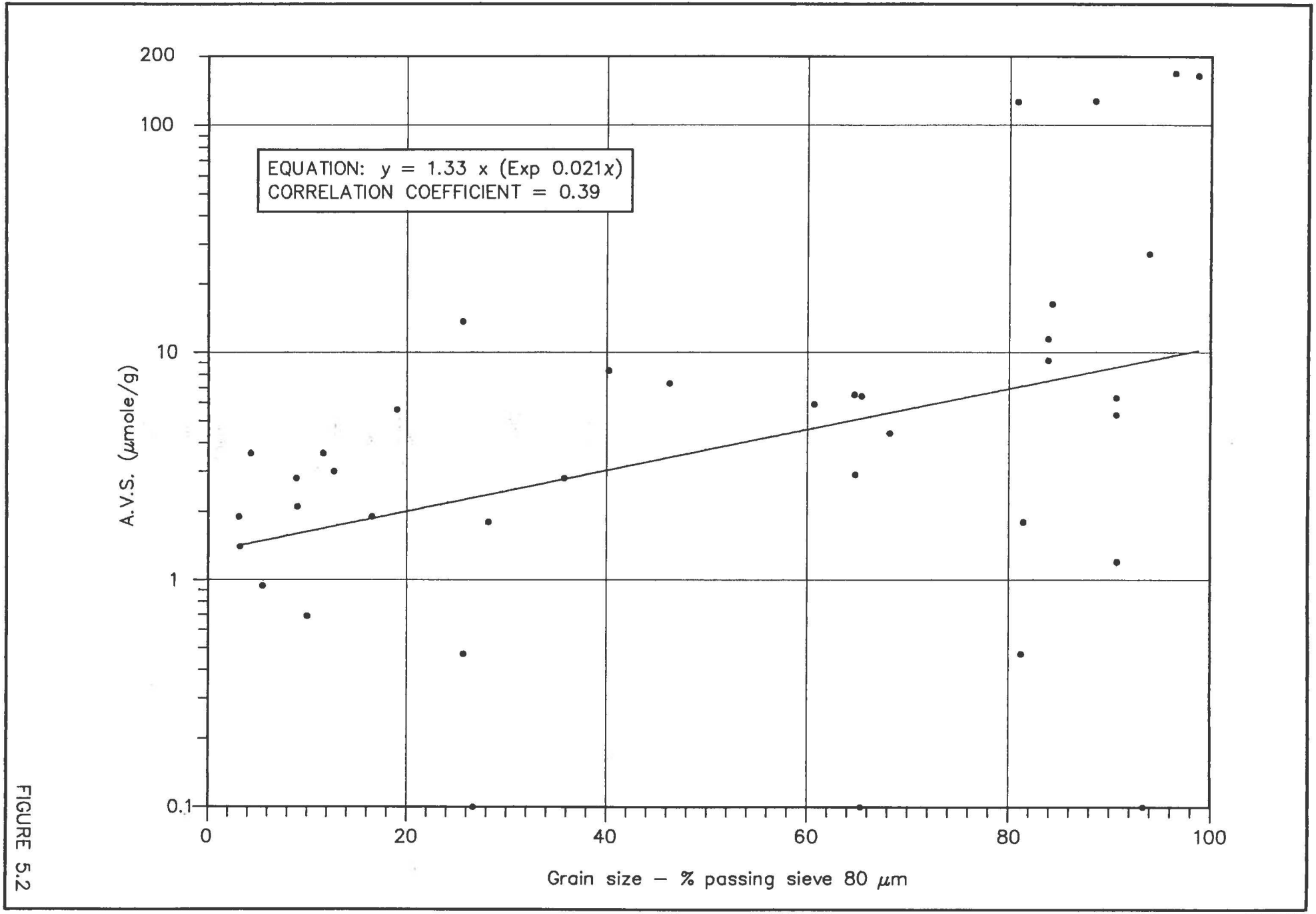


FIGURE 5.2

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ALLIED–SIGNAL INC. – CLARK ISLAND SITE
GRANDE–ILE SEDIMENTS CHARACTERIZATION
CORRELATION BETWEEN TOTAL CADMIUM CONCENTRATIONS AND SIMULTANEOUSLY EXTRACTED CADMIUM IN SEDIMENTS

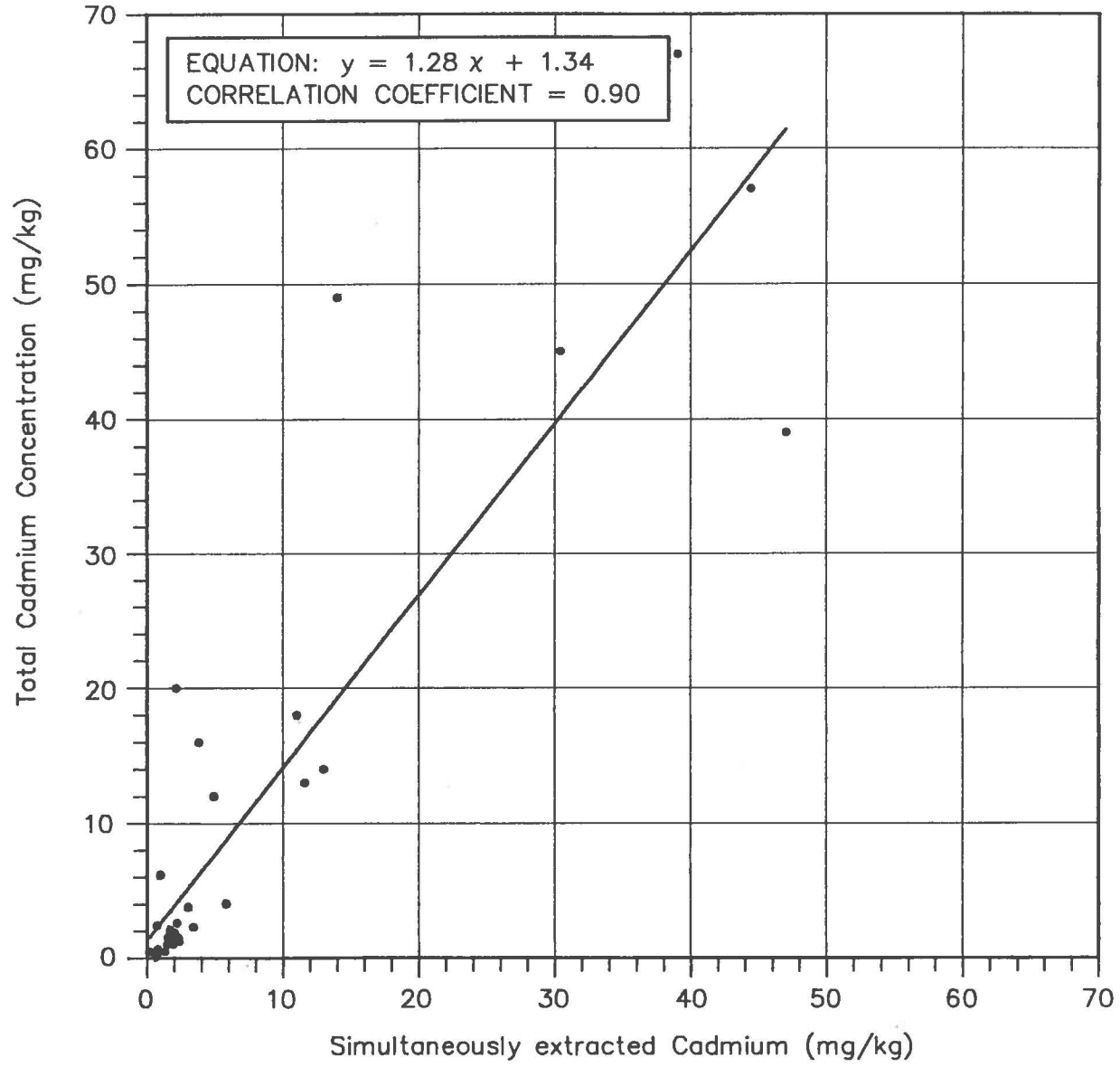


FIGURE 5.3

ALLIED–SIGNAL INC. – CLARK ISLAND SITE
GRANDE–ILE SEDIMENTS CHARACTERIZATION
CORRELATION BETWEEN TOTAL COPPER CONCENTRATIONS AND SIMULTANEOUSLY EXTRACTED COPPER IN SEDIMENTS

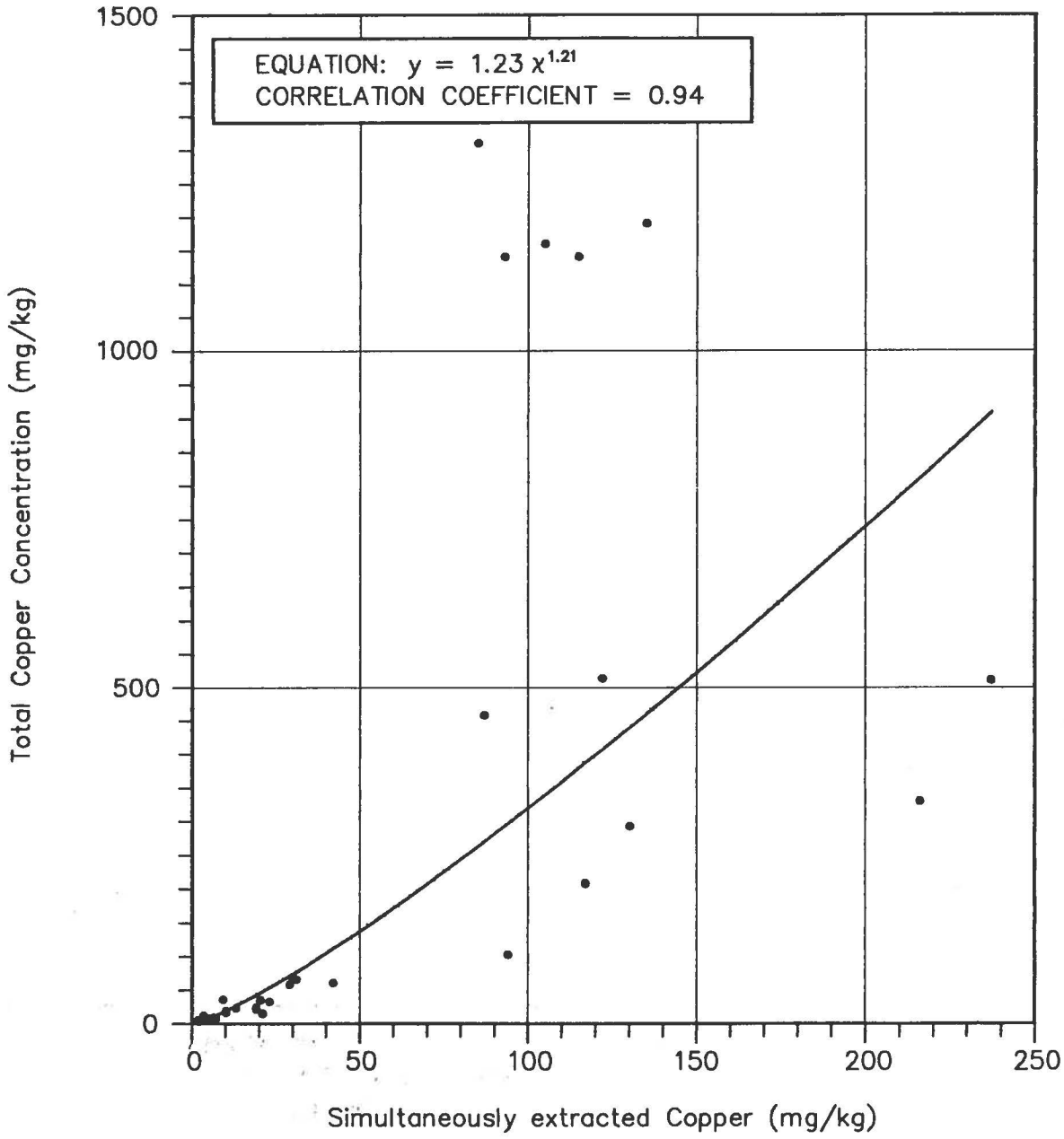


FIGURE 5.4

ALLIED–SIGNAL INC. – CLARK ISLAND SITE
GRANDE–ILE SEDIMENTS CHARACTERIZATION
CORRELATION BETWEEN TOTAL ZINC CONCENTRATIONS AND SIMULTANEOUSLY EXTRACTED ZINC IN SEDIMENTS

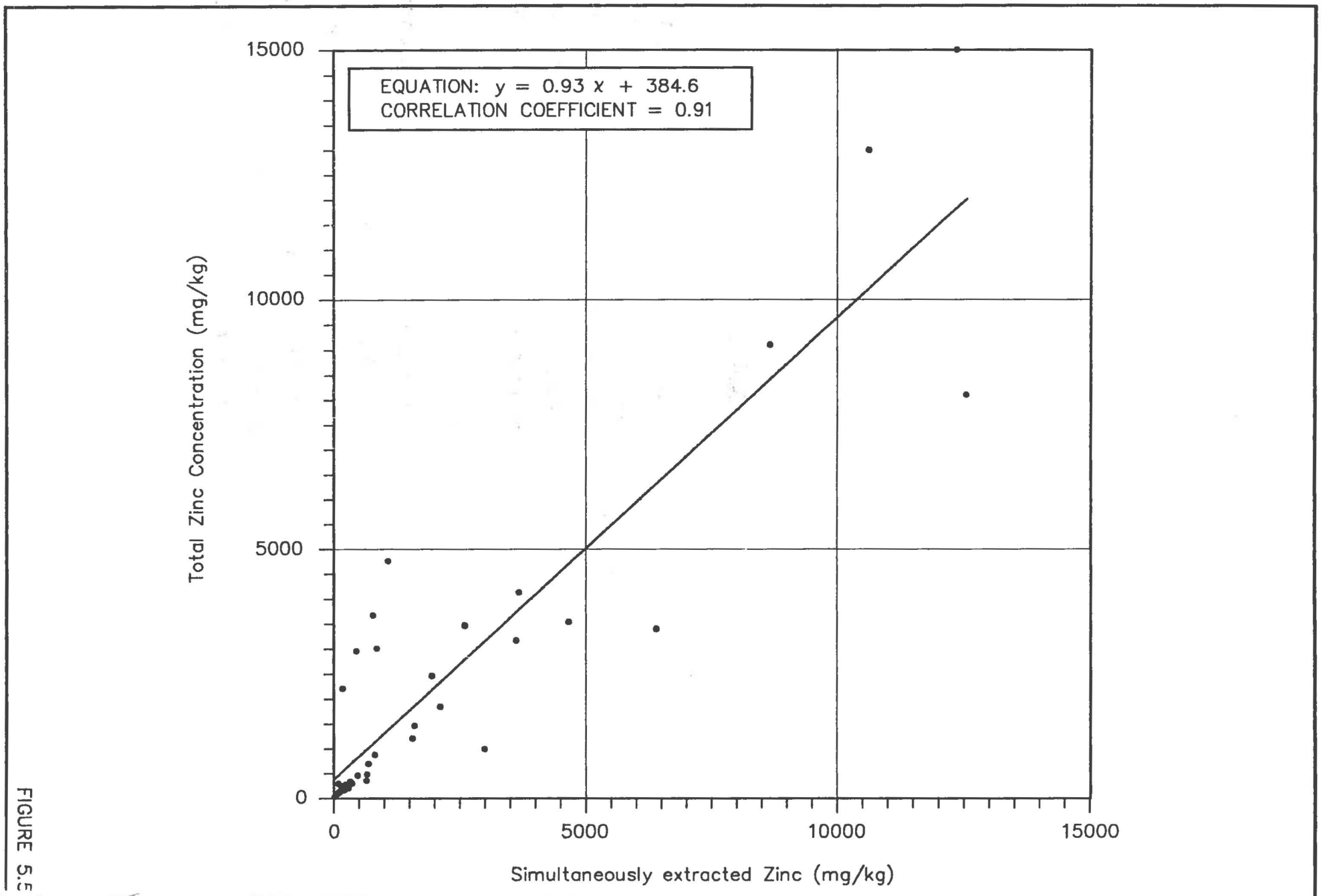


FIGURE 5.5

It should be noted that the concentration measurements for each of the two analytical methods were performed on different samples obtained at the same location. As mentioned previously, the toxicity test require that the sample should not be in contact with ambient air. In order to fulfil this requirement, two different samples were collected at the same location. The first sample was analyzed for the total metal concentrations and the second sample was analyzed for the simultaneously extracted metals.

In conclusion, considering that the analytical methods for each laboratory are different and that the analyzed samples are not split samples, the results obtained for each metal are considered acceptable since the concentration values measured by both methods are in the same range.

6.0 SUMMARY AND CONCLUSIONS

In order to develop a preliminary understanding of their toxicity, tests were carried out on sediments collected along Grande-Ile shoreline (Priority Zone II) and along North-West shoreline of Clark Island (Priority Zone I). These tests were realized in order to assess on a preliminary basis the bioavailability of metals in sediments and to select stations where eventual sediments bioassays would need be performed.

The toxicity assessment tests were based on the AVS methodology recently developed by Ditoro D. et al. A draft analytical method issued by EPA was used to determine the Acid Volatile Sulfides (AVS) and Simultaneously Extracted Metals (SEM) in sediments. The SEM was determined for the four (4) main heavy metals commonly found in Clark Island sediments. According to Ditoro D. et al., when the ration $\sum$SEM/AVS exceeds 1.0, toxicity potentially appears.

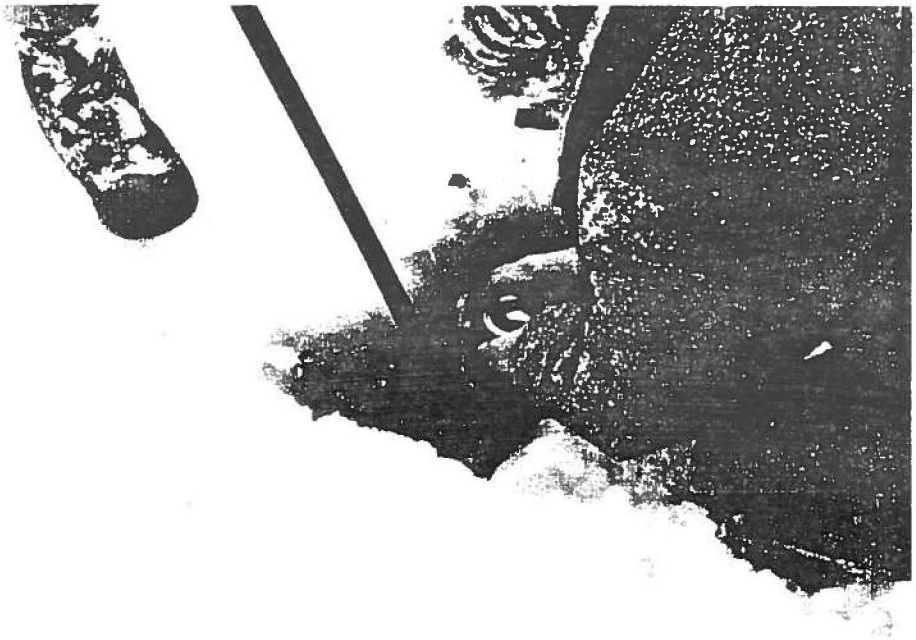
The results of these tests have been summarized in Table 5.1. According to the test results, it appears that the majority of the sediment samples may be toxic for benthic organisms. Three different zones can be identified along the Grande-Ile shoreline, and were illustrated in Figure 5.1.

According to these zones, the following conclusions may be formulated. In the areas where the ratio ∑SEM/AVS is below 1.0 or exceeds 1.0 but is below 3.0 and where the total metals concentrations are important, the sediments grain size and corresponding Sulfides content explain the low toxicity. Also, for low toxicity areas (<1.0, or from 1.0 to 3.0), the situation is explained by the insignificant presence of heavy metals. In the areas where the ratio ∑SEM/AVS exceeds 3.0, the total metals concentrations are important and exceed MENVIQ level 3 criteria.

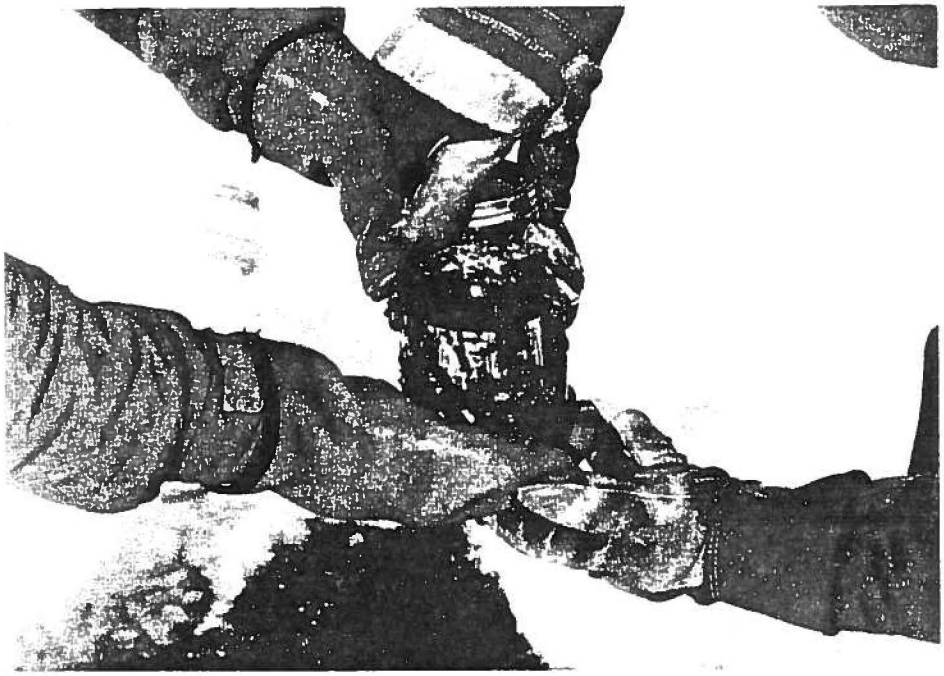
Considering the preliminary toxicity assessment results, sediments bioassays would be needed to assess bioavailability of metals and determine whether the sediments in Priority Zone II exhibit any aquatic toxicity. Such bioassays should be performed on samples from areas where high SEM/AVS ratio were obtained.

APPENDIX A

PHOTOGRAPHIES



GRANDE-ILE SHORELINE SEDIMENTS CHARACTERIZATION
SAMPLE COLLECTION FOR THE AVS AND SEM ANALYSES



GRANDE-ILE SHORELINE SEDIMENTS CHARACTERIZATION
SAMPLE COLLECTION FOR THE AVS AND SEM ANALYSES
FROM STATION SE-93-81 LOCATED AT THE NORTHERN TIP
OF CLARK ISLAND

APPENDIX B

DRAWINGS

GRANDE–ILE

CLARK ISLAND/
ÎLE AUX CHATS

5 013 600
253 200
5 013 400
5 013 200
253 400
5 013 000
5 012 800
253 400
253 200
5 012 600
253 000

LEGEND/LÉGENDE :

SC-93-02 (A) SURFACE SEDIMENTS SAMPLING STATION WITH TOXICITY TESTS / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS AVEC ANALYSES DE TOXICITÉ

SC-93(124) □ SURFACE SEDIMENTS SAMPLING STATION/

CLARK ISLAND/
ÎLE AUX CHATS

5 012 600

253 000

252 800

252 600

5 013 200

5 013 000

5 012 800

5 012 600

5 012 400

LEGEND/LÉGENDE :

SE-93-02 — SURFACE SEDIMENTS SAMPLING STATION WITH TOXICITY TESTS / STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS AVEC ANALYSES DE TOXICITÉ

SE-93(124) — SURFACE SEDIMENTS SAMPLING STATION/ STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (JANUARY/JANVIER 1993)

SE-90-13 — SEDIMENTS BOREHOLE/ FORAGE AU TRAVERS DES SÉDIMENTS (FEBRUARY/FÉVRIER 1990)

SE-90-114 — SURFACE SEDIMENTS SAMPLING STATION/ STATION D'ÉCHANTILLONNAGE DE SURFACE (JUNE/JUIN 1990)

SE-93-01 — SURFACE SEDIMENTS SAMPLING STATION/ STATION D'ÉCHANTILLONNAGE DES SÉDIMENTS DE SURFACE (FEBRUARY/FÉVRIER 1993)

SE-93-86 — SAMPLING STATION WHERE NO SEDIMENTS WERE RECOVERED / STATION D'ÉCHANTILLONNAGE DES SÉDIMENT DE SURFACE SANS RÉCUPÉRATION (FEBRUARY/FÉVRIER 1993)

0 20 40 m

1:3000

Seal Signal

TECSULT — Tecsult Inc.

SURFACE SEDIMENT SAMPLING STATION WITH TOXICITY TESTS

M.G.M. | P.A. | M.G.M.

APRIL 199 | 4381 | FIGURE 2.1

252 800

5 014 400

5 014 200

253 000

5 014 000

5 013 800

5 013 600

253 200

GRANDE–

252 600

252 400

252 000

BED ROCK

BED ROCK

BED ROCK

BED ROCK

252 100

252 000

BED ROCK

BED ROCK

BED ROCK

BED ROCK

252 000

5 014 200

252 000

5 014 000

5 013 800

5 013 600

SÉRIGNY
ISLAND

5 013 400

5 013 200

APPENDIX C

EPA draft analytical method for determination of acid volatile sulfides and simultaneously extracted metals in sediment

United States
Environmental Protection Agency
Office of Water

Office of Science and Technology
Health and Ecological Criteria Div.
Washington, DC 20460

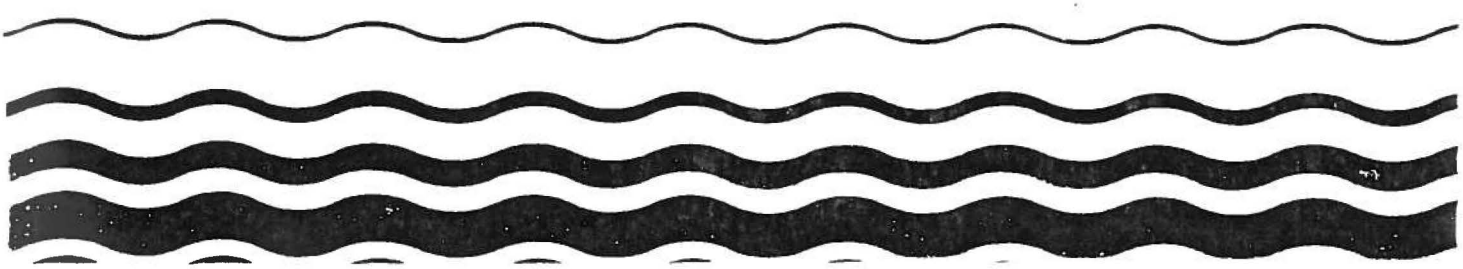
EPA xxx/x-xx-xxx
August 1991

WATER

Draft Analytical Method

for Determination of Acid

Volatile Sulfide in Sediment



DETERMINATION OF ACID VOLATILE SULFIDES AND SIMULTANEOUSLY EXTRACTABLE METALS IN SEDIMENT

April, 1991

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DETERMINATION OF ACID VOLATILE SULFIDES AND SIMULTANEOUSLY EXTRACTABLE METALS IN SEDIMENT

1. SCOPE AND APPLICATION

1.1 This method describes procedures for the determination of acid volatile sulfides (AVS) and for metals that are solubilized during the acidification step (simultaneously extracted metal, SEM). The conditions used have been reported to measure amorphous or moderately crystalline monosulfides (1). As a precipitant of toxic heavy metals, sulfide is important in controlling the bioavailability of metals in anoxic sediments (2). If the molar ratio of toxic metals measured by SEM to AVS exceeds one, the metals are potentially bioavailable. Because the relative amounts of AVS and SEM are important in the prediction of potential metal bioavailability, it is important to use the SEM procedure for sample preparation for metal analysis. This uses the same conditions for release of both sulfide and metal from the sediment and thus provides the most predictive means of assessing the amount of metal associated with sulfide.

2. SUMMARY OF METHOD

2.1 The AVS in the sample is first converted to hydrogen sulfide (H_2S) by acidification with hydrochloric acid at room temperature. The H_2S is then purged from the sample and trapped. The amount of sulfide that has been trapped is then determined. The SEM are metals liberated from the sediment during the acidification. These are determined after filtration of the sample.

2.2 Two types of apparatus for sample purging and trapping of H_2S are described. One uses a series of Erlenmeyer flasks while the other uses flasks and traps with ground glass stoppers. The former is less costly. The latter is less prone to leakage that causes low recovery of AVS. The latter is recommended when higher degrees of precision are desired and for samples containing low levels of AVS.

2.3 Three means of quantifying the H_2S released by acidifying the sample are provided. In the gravimetric procedure, the H_2S is trapped in silver nitrate. The silver sulfide that is formed is determined by weighing (2,3). This procedure is recommended for samples with moderate or high AVS concentrations. In the colorimetric method, the H_2S is trapped in sodium hydroxide. The sulfide is converted to methylene blue that is measured (4). This procedure is recommended for samples that have low to moderate AVS concentrations. In an alternative procedure the H_2S is trapped in an antioxidant buffer before using an ion-selective electrode (5,6).

2.4 After release of the H_2S, the acidified sediment sample is membrane filtered before determination of the SEM by atomic absorption or inductive coupled plasma spectrometic methods (7,8).

3. DEFINITIONS

3.1 ACID VOLATILE SULFIDES (AVS) - Amorphous, moderately crystalline monosulfides, and other sulfides that form hydrogen sulfide under the conditions of this test.

3.2 SIMULTANEOUSLY EXTRACTED METALS (SEM) - Metals, commonly cadmium, copper, lead, mercury, nickel and zinc, which form less soluble sulfides than do iron or manganese, and which are at least partially soluble under the conditions of this test.

3.3 METHOD DETECTION LIMIT (MDL) - The minimum concentration of an analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined from the analysis of a sample that contains the analyte within a given matrix.

3.4 LABORATORY REAGENT BLANK (LRB) - An aliquot of reagent water or reagents that is treated exactly as a sample including exposure to all glassware, equipment, and reagents that are used with samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents or apparatus.

3.5 STOCK STANDARD SOLUTION - A concentrated solution of the analyte prepared in the laboratory using assayed reference compounds or purchased from a reputable commercial source.

3.6 CALIBRATION STANDARDS (CAL) - Solutions prepared from the stock standard solution that is used to calibrate the method response with respect to analyte concentration.

3.7 LABORATORY FORTIFIED BLANK (LFB) - An aliquot of reagent water or reagents to which a known quantity of the method analyte is added in the laboratory. The LFB is analyzed exactly like a sample. Its purpose is to determine whether the method is within accepted control limits.

3.8 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) - An environmental sample to which a known quantity of the method analyte is added in the laboratory. The LFM is analyzed exactly line a sample. Its purpose is to determine whether the sample matrix contributes bias to the analytical results.

4. INTERFERENCES

4.1 Oxygen in the reagents and apparatus is the primary interference reported. Special precautions must be taken to insure that the analytical system is adequately purged with oxygen-free nitrogen. Argon may be substituted for nitrogen if it is important that an even lower level oxygen concentration be maintained (4).

4.2 The pH of the sample after the addition of the acid and during the purge process must be below 3. Typically, the pH is below 2.

5. SAFETY

5.1 The toxicity or carcinogenicity of reagents used in this method have not been fully established. Each chemical and environmental sample should be regarded as a potential health hazard and exposure should be minimized. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should be available to all personnel involved in the chemical analysis.

5.2 Hydrogen sulfide is a highly poisonous, gaseous compound having a characteristic odor of rotten eggs. It is detectable in air by humans at a concentration of approximately 0.002 ppm. Handling of acid samples should be performed in a hood or well ventilated area. If hydrogen sulfide is detected in the air by the laboratory staff, sample handling procedures must be corrected.

6. APPARATUS AND EQUIPMENT

6.1 Glassware

6.1.1 AVS evolution and H_2S trapping - Glassware in Section 6.1.1.1 is recommended. Glassware in Section 6.1.1.2 may be used, but will not provide as high precision or accuracy for samples.

6.1.1.1 For highest precision and low AVS levels - For each analytical train 500 mL gas washing bottles, one 250 mL round bottom flask with a septum (Ace Glass 6934 or equivalent), 100 or 250 mL impingers. The round bottom flask contains the sediment and acid is introduced to it by a syringe inserted through the septum. The flasks are connected by plastic tubing. In all cases the inlets are below the liquid level and the outlets are above the liquid levels. The apparatus is assembled as shown in Figure 1 and more than one analytical train can be connected to a single cylinder of nitrogen if flow controllers are installed in the

line. Different amounts of glassware are required for each of the three means of sulfide determination.

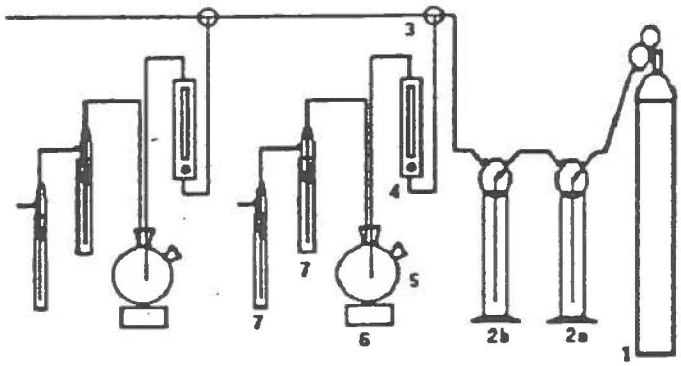

Figure 1. Apparatus for AVS determination: 1.N_2 cylinder; 2.Gas washing bottles: (a) oxygen scrubbing solution, (b) deionized water; 3.Three-way stopcock; 4.Purge flow controller; 5.Reaction flask; 6.Magnetic stirrer; 7.Sulfide traps.

6.1.1.2 For routine analysis - Erlenmeyer flasks, 250 mL, are substituted for the gas washing bottle, the round bottom flask and the impingers. The flask size should be consistent with sample size and reagent volumes. A thistle tube fitted with a stopcock or a separatory funnel is provided to introduce acid to the flask containing the sediment sample. This flask is fitted with a three hole stopper. One hole is for the thistle tube or separatory funnel and the other two are for the gas inlet and outlet. The other flasks are fitted with two hole stoppers; one hole is for the gas inlet and the other is for the gas outlet. The gas inlets are below the liquid level and the gas outlets are above the liquid level. The flasks are connected by plastic tubing.

6.1.2 Evaporating dishes, porcelain, 100 mL.

6.1.3 Assorted calibrated pipettes and volumetric flasks.

6.2 Drying oven - Capable of maintaining a constant temperature in the range of 100-104°C.

6.3 Analytical balance - of weighing to 0.0001 g.

6.4 Magnetic stirrer, thermally insulated, and Teflon-coated stirring bar.

6.5 Gravimetric method

6.5.1 Filtering flask.

6.5.2 Filter holder for 47 mm filter.

6.6 Colorimetric method

6.6.1 Spectrophotometer - Capable of measuring absorbance at 670 nm.

6.6.2 Spectrophotometer cells.

6.7 Ion-selective electrode method

6.7.1 Electrometer, pH meter or ion-selective meter - Compatible with the use of ion-selective electrodes.

6.7.2 Sulfide selective electrode.

6.8 Atomic absorption or inductive couple plasma spectrophometer for the determination of SEM.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 All water and reagents used in this method must be free of dissolved oxygen and sulfides. Freshly prepare and use deaerated, deionized water, DDIW, by purging dissolved oxygen from the deionized water by vigorously bubbling with oxygen free nitrogen for approximately one hour. Deaerate reagents by purging with nitrogen.

7.2 Sodium sulfide standard - Required for quality assurance and calibration.

7.2.1 Sulfide stock standard solution, approximately 0.05M or 50 µmoles/mL.

7.2.1.1 Place a few crystals of $Na_2S \cdot 9H_2O$ in a beaker. Wash them with distilled water and dry them by blotting with filter paper. Weigh about 12 gram of $Na_2S \cdot 9H_2O$ and dissolve it in 1,000 mL of DDIW. Store in a brown bottle.

7.2.1.2 Standardize against thiosulfate solution.

7.2.1.2.1 Pipette 10.00 mL of 0.025N standard iodine solution (Section 7.2.2) into each of two 125-mL Erlenmeyer flasks.

7.2.1.2.2 Pipette 2.00 mL of sulfide stock standard solution into one flask. Pipette 2.00 mL of DDIW, as a laboratory reagent blank, into the other flask.

7.2.1.2.3 Add 5.00 mL of 6M HCl into each flask, swirl slightly, then cover and place in the dark for 5 minutes.

7.2.1.2.4 Titrate each with 0.025N thiosulfate (Section 7.2.3), adding soluble starch indicator when the yellow iodine color fades. The end point is reached when the blue color disappears.

7.2.1.2.5 Calculate the sulfide concentration as follows:

$$\text{Sulfide } (\mu\text{mol / mL}) = \frac{(T_{blank} - T_{sample}) \times N_{S_2O_3^{2-}}}{V_{sample}} \times \frac{1 \text{ mole } S^{2-}}{2 \text{ equiv } S^{2-}} \times \frac{1000 \text{ } \mu\text{moles}}{1 \text{ mmole}}$$

where T = volume of titrant used for the blank and sample (mL)

N = concentration of $S_2O_3^{2-}$ titrant

V = volume of sample used (2.00 mL)

7.2.2 Standard iodine solution, 0.025N - Dissolve 20 to 25 gram potassium iodide, KI, in a small volume of deionized water, add 3.2 gram iodine, and dilute to 1,000 mL. Standardize against 0.025N sodium thiosulfate (Section 7.2.3) using starch solution as indicator.

7.2.3 Standard sodium thiosulfate solution, 0.025N. May be purchased commercially or prepared in the laboratory. If prepared in the laboratory, it should be standardized against potassium dichromate.

7.2.3.1 Weigh approximately 6.2 g of sodium thiosulfate, $Na_2S_2O_3 \cdot 5\ H_2O$, into a 500 mL beaker. Add 0.1 g sodium carbonate, Na_2CO_3, and dissolve in 400 mL deionized water. Pour into a 1.0 L volumetric flask and dilute to volume with deionized water.

7.2.3.2 Standardize against potassium dichromate, K_2CrO_7.

7.2.3.2.1 Accurately weigh approximately 0.2 g dry K_2CrO_7 and place in a 500 mL Erlenmeyer flask. Dissolve in 50 mL deionized water.

7.2.3.2.2 Dissolve 3 g of potassium iodide, KI, in 50 mL distilled water, add 5 mL of 6M HCl, and add to KI solution. Swirl, cover and store in the dark for 5 minutes. Add 200 mL deionized water and titrate with the thiosulfate solution, adding starch indicator when the yellow iodine color fades, until the blue color turns to pale green.

7.2.3.2.3 Calculate the thiosulfate concentration as follows:

$$N\left(S_2O_3^{2-}\right) = \frac{g\ K_2CrO_7}{mL\ S_2O_3^{2-}} \times \frac{1\ mole\ K_2CrO_7}{294.19\ g\ K_2CrO_7} \times \frac{6\ equiv\ K_2CrO_7}{1\ mole\ K_2CrO_7} \times \frac{1000\ mL}{1\ L}$$

7.2.4 Starch indicator - Dissolve 1.0 gram soluble starch in 100 mL boiling deionized water.

7.2.5 Sulfide working standards - Prepare sulfide working standards using the sulfide stock standard solution in Section 7.2.1. The concentrations of the following standards will depend on the exact concentration of the sulfide stock standard determined in Section 7.2.1.2.5. Correct concentrations of the the standards in the following part of this section and the amount of sulfide in standards used in the colorimetric method in Section 12.2.5 by multiplying by a factor of the concentration determined in Section 7.2.1.2.5 divided by 50 µmoles/mL.

7.2.5.1 Prepare sulfide working standard A by diluting 1.00 mL of sulfide stock standard to 100.0 mL. This solution contains 0.5 µmole sulfide/mL, if the concentration of the sulfide stock standard is exactly 0.05M.

7.2.5.2 Prepare sulfide working standard B by diluting 10.00 mL of sulfide stock standard to 100.0 mL. This solution contains 5.0 µmole sulfide/mL, if the concentration of the sulfide stock standard is exactly 0.05M.

7.3 AVS evolution

7.3.1 Hydrochloric acid 6M - Dilute 500 mL of concentrated hydrochloric acid (sp. gr. 1.19) to 1L with deionized water.

7.3.2 Nitrogen gas, oxygen free, with regulator and flow controller. An oxygen gas scrubber may be required and is available commercially or deoxygenating solutions may be placed in the flask or gas washing bottle placed first in the analytical train.

7.3.3 Plastic hypodermic syringe, 30 mL, and needle.

7.4 Gravimetric method

7.4.1 Potassium acid phthalate, 0.05M - Dissolve 10.2 g of potassium acid phthalate, $KHC_8H_4O_4$, in DDIW and dilute to 1L.

7.4.2 Silver nitrate, 1M - Dissolve 17 g of silver nitrate, $AgNO_3$, in DDIW and dilute to 1L. Store in a dark bottle.

7.4.3 Glass fiber filters, 1.2 micron - Predry filters at 102°C.

7.5 Colorimetric method

7.5.1 Sodium hydroxide solution, 1M - Dissolve 40 g sodium hydroxide in 1000 mL DDIW.

7.5.2 Sodium hydroxide solution, 0.5M - Dissolve 20 g sodium hydroxide in 1000 mL DDIW.

7.5.3 Mixed diamine reagent, MDR

7.5.3.1 Component A - Add 660 mL concentrated sulfuric acid to 340 mL of DDIW. After the solution cools, dissolve 2.25 g N-N-dimethy-p-phenylenediamine oxalate in it.

7.5.3.2 Component B - Dissolve 5.4 g ferric chloride hexahydrate ($FeCl_3 \cdot 6 H_2O$) in 100 mL concentrated hydrochloric acid and dilute to 200 mL with DDIW.

7.5.3.3 Mixed diamine reagent, MDR - Mix components A and B.

7.5.4 Sulfuric acid solution, 1.0M - Dilute 56 mL concentrated sulfuric acid (H_2SO_4) to 1 L with DDIW.

7.6 Ion-selective electrode method

7.6.1 Sodium hydroxide solution - Dissolve 80 g of sodium hydroxide in 700 mL of DDIW with caution. Cool to room temperature.

7.6.2 Sulfide anti-oxidant buffer (SAOB) - To the sodium hydroxide solution in Section 7.6.1 add and dissolve 74.45 g of disodium ethylenediaminetetraacetic acid and 35.23 g of ascorbic acid. Dilute to 1L with DDIW.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Sulfide ion is unstable in the presence of oxygen. Protect sediment samples from exposure to oxygen during sample collection and storage.

8.2 During storage sulfides can be formed or lost due to biological activity and sulfide can be lost by volatilization or oxidation. Metal speciation can change as a result of changes in sulfide concentration and as a result of other changes in the sample.

8.3 Samples should be collected in wide mouth jars with a minimum of air space above the sediment. If possible, the headspace should be purged with oxygen free nitrogen. The jars must have Teflon or polyethylene liners.

8.4 Samples should be cooled to 4°C as soon as possible after collection. Samples maintained at 4°C have been found to have no significant loss of AVS for storage periods up to 2 weeks (4). Anoxic sediments stored at 4°C for 20 days show significant changes in metal partitioning, suggestive of oxidation of the sediment (9). Holding time for samples should not exceed 14 days.

9. CALIBRATION AND STANDARDIZATION

9.1 Calibrate the photometer with a minimum of four standards and a blank that cover the expected range of the samples. Prepare a calibration graph relating absorbance to the µmoles of sulfide taken.

9.2 Calibrate the sulfide electrode system with a minimum of three standards that cover the expected range of the samples. Standards must be made up in SAOB diluted 1+1 with DDIW. Follow the manufacturer's instructions for use of the electrode.

9.3 Overall sulfide recovery is determined by analysis of a known amount of sodium sulfide standard added to DDIW from which the sulfide is liberated in the analysis train (LFB). Recoveries of 95% ± 10% are expected.

10. QUALITY CONTROL

10.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirement of this program consists of an initial demonstration of laboratory capability, and the analysis of laboratory reagent blanks, fortified blanks and samples as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of data thus generated.

10.2 INITIAL DEMONSTRATION OF PERFORMANCE

10.2.1 The initial demonstration of performance is used to characterize instrument performance, method detection limits, and linear calibration ranges.

10.2.2 Method detection limit (MDL) - The method detection limit should be established for the analyte, using DDIW (blank) fortified at a concentration two to five times the estimated detection limit (10). To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = t \times s$$

where, t = students' t value for a 99% confidence level and a standard deviation

estimate with n-1 degrees of freedom (t = 3.14 for seven replicates), and

s = standard deviation of the replicate analyses.

Method detection limits should be determined every six months or whenever a significant change in background or instrument response is expected.

10.2.3 Linear calibration ranges - The upper limit of the linear calibration range should be established by determining the signal responses from a minimum of four different concentration standards covering the expected range, one of which is close to the upper limit. The linear calibration range that may be used for the analysis of samples should be judged by the analyst from resulting data. Linear calibration ranges should be determined every six months or whenever a significant change in instrument response may be expected.

10.3 ASSESSING LABORATORY PERFORMANCE - REAGENT AND FORTIFIED BLANKS

10.3.1 Laboratory reagent blank (LRB) - The laboratory must analyze at least one reagent blank (3.4) with each set of samples. Reagent blank data are used to assess contamination from the laboratory environment and reagents. If an analyte value in the reagent blank exceeds its determined MDL, then laboratory or reagent contamination should be suspected. Any determined source of contamination should be corrected and the samples reanalyzed.

10.3.2 Laboratory fortified blank (LFB) - The laboratory must analyze at least one fortified blank (3.7) with each batch of samples. Calculate accuracy as percent recovery. If the recovery of the analyte falls outside the control limits (see 10.3.3), the analyte is judged to be out of control, and the source of the problem should be identified and resolved before continuing analyses.

10.3.3 Until sufficient data become available from within their own laboratory (usually a minimum of twenty to thirty analyses), the laboratory should assess laboratory performance against recovery limits of 85-105%. When sufficient internal performance data becomes available, develop control limits from the mean recovery (x) and the standard deviation (s) of the mean recovery. These data are used to establish upper and lower control limits as follows:

UPPER CONTROL LIMIT = $x + 3s$

LOWER CONTROL LIMIT = $x - 3s$

After each five to ten new recovery measurements, new control limits should be calculated using only the most recent twenty to thirty data points.

10.4 ASSESSING ANALYTE RECOVERY - LABORATORY FORTIFIED SAMPLE MATRIX

10.4.1 The laboratory must fortify a minimum of 10% of the routine samples or one fortified sample per set, whichever is greater. Ideally, the concentration should at least double the background concentration. Over time, samples from all routine sample sources should be fortified.

10.4.2 Calculate the percent recovery for the analyte, corrected for background concentrations measured in the unfortified sample, and compare these values to the control limits established in Section 10.3.3 for the analyses of LFBs. Spike recovery calculations are not required if the spike concentration is less than 10% of the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{(C_s - C_b)}{S} \times 100$$

where

R = percent recovery,

C_s = fortified sample concentration,

C_b = sample background concentration, and

S = concentration equivalent of the fortified sample.

10.4.3 If the recovery of the analyte in the fortified sample falls outside the designated range, and the laboratory performance on the LFB for the analyte is shown to be in control (Section 10.3) the recovery problem encountered with the fortified sample is judged to be matrix related, not system related.

11. GENERATION OF H_2S

11.1 Assemble glassware according to the detection method to be used. The setup in Figure 1 should be followed as a general guide. In all cases a flask or gas washing bottle containing a deoxygenating solution may be placed in the sample train between the nitrogen tank and the first flask. Glassware is specified in Section 6.1.1. It is recommended that nitrogen be controlled by a flow controller, but an equivalent flow rate may be regulated by a clamp and bubble rate determined. In all cases the glassware will minimally consist of a H_2S generating flask and a series of traps.

11.1.1 Gravimetric method - The first flask contains the sediment sample or standard. The second flask contains 175-200 mL of potassium hydrogen phthalate reagent

7.4.1 as an HCl trap. The third and fourth flasks contain 175-200 mL of silver nitrate reagent 7.4.2. If glassware specified in Section 6.1.1.1 is used, the second flask is a gas washing bottle and the third and fourth flasks are impingers.

11.1.2 Colorimetric method - The first flask contains the sediment sample or standard. The second and third flask contain an absorbant of 80 mL 0.5M NaOH reagent 7.5.2. If glassware specified in Section 6.1.1.1 is used, the second and third flasks are impingers.

11.1.3 Ion-selective electrode method - The first flask contains the sediment sample or standard. The second and third flask contain an absorbant of 50 mL SAOB reagent 7.6.2 and 30 mL DDIW. If glassware specified in Section 6.1.1.1 is used, the second and third flasks are impingers.

11.2 One hundred milliliters (100 mL) of DDIW, minus the volume of water contained in the wet sediment sample in Section 11.3, and a magnetic stirring bar are added to the flask that will contain the sediment. For the computation of the volume of water contained in the wet sediment, see Section 13.3. The traps are filled and deaerated by bubbling nitrogen for 10 minutes at a flowrate of 100 cm^3/min. Reduce flow to 40 cm^3/min.

11.3 Weigh approximately 10 g of wet sediment. If AVS concentration is high, a smaller amount of sediment may be required; use of sediment samples smaller than 1-2 grams is not recommended due to sulfide oxidation and sample heterogeneity. Use of large sediment samples is not recommended because significant amounts of acid may be neutralized. Place sediment in the standard taper round bottom flask or the Erlenmeyer flask fitted with the thistle tube or separatory funnel. Parafilm has been found to be free of sulfide (4). Samples may be weighed on 2 × 2 inch pieces of parafilm and the parafilm and sample introduced to the flask. Rinsing the sample into the flask is not recommended. Purge the sample for 10 minutes at a nitrogen flowrate of 40 cm^3/min. Stop the flow of nitrogen.

11.4 Using a 30 mL syringe, inject 20 mL of 6M HCl, which has been bubbled with N_2 gas for 30 minutes, into the reactor through the septum. If the apparatus described in Section 6.1.1.1 is used, add the HCl from the thistle tube or the separatory funnel. Bubble N_2 through the sample for 1 hour at a flowrate of 20 cm^3/min and magnetically stir the sample at the same time.

11.5 Analyze sulfide contained in sulfide trap by the appropriate analytical procedure in Section 12.

12. ANALYSIS OF SULFIDE

12.1 Gravimetric method

12.1.1 Insure that the final trap, the second silver nitrate trap, contains no precipitate.

12.1.2 Filter the silver sulfide contained in the first sulfide trap through a preweighed 1.2 micron filter. Dry at 102 °C and weigh.

12.1.3 Calculate the amount of silver sulfide as the difference between the weight of silver sulfide and the filter and the weight of the predried filter.

12.1.4 Calculate the amount of sulfide in the sample:

$$\text{Sulfide in wet sediment } (\mu\text{moles}) = \frac{\text{g } Ag_2S}{247.8} \times 10^6$$

12.2 Colorimetric method

12.2.1 If the AVS concentration is low, add 10 mL of the mixed diamine reagent (MDR) directly to the NaOH solution in each trap tube to develop the color. Transfer this solution to a 100 mL volumetric flask and dilute to the mark with DDIW. If the sulfide contained in the NaOH in the tube trap exceeds 18 µmoles, transfer the NaOH in each tube trap to a 100 mL volumetric flask. Rinse the trap with deaerated 0.5M NaOH and dilute to volume with NaOH. An appropriate volume aliquot of this solution is used for the analysis. In this case, the aliquot is transferred to a 100 mL. Sufficient 0.5M NaOH is added so that the total volume is 80 mL, 10 mL MDR is added and the solution is diluted to 100 mL with DDIW. Use of sediment samples smaller than 1-2 grams is not recommended due to sulfide oxidation and sample heterogeneity.

12.2.2 After 30 minutes, measure the absorbance of light at 670 nm using a half-inch diameter or 1 cm rectangular spectrophotometer cell.

12.2.3 If the absorbance of the sample is greater than 0.6, dilute 10-fold with 1.0M H_2SO_4 and compare to the high range calibration curve.

12.2.4 Normally, the sulfide concentration in second trap tube is close to the blank value in this procedure and is not significant in calculating the concentration of sulfide. If a significant color is developed, the flow rate and amount of sulfide in the standard or sediment should be checked

12.2.5 Preparation of calibration curve - The indicated amounts of sulfide are based on a 0.05 M concentration of the sulfide stock standard solution. The procedure indicated in Section 7.2.5 should be used to calculate the exact amount of sulfide in each of the standards.

12.2.5.1 Low range calibration curve - 0.0 - 2.5 µmoles S^{2-} (0.0 - 80 µg S^{2-})

Add 80 mL 0.5 N sodium hydroxide to each of a series of 100 mL of flasks and add 0.00, 1.00, 2.00, 3.00, 4.00, and 5.00 mL of sulfide working standard A to these flasks. These samples contain 0.00, 0.50, 1.00, 1.50, 2.00, and 2.50 µmoles S^{2-}, respectively. Add 10.0 mL of MDR to each and dilute to 100.00 mL with deionized water. After 30 minutes, measure the absorbance at 670 nm.

12.2.5.2 High range calibration curve - 0.0 - 20.0 µmoles S^{2-}

(0.0 - 640 µg S^{2-})

Add 80 mL 0.5M sodium hydroxide in 100 mL flasks and add 0.00, 1.00, 2.00, 3.00 and 4.00 mL of sulfide working standard B to these flasks. These samples contain 0.0, 5.00, 10.00, 15.00, and 20.00 µmoles S^{2-}, respectively. Add 10.0 mL of MDR and dilute to 100.00 mL with deionized water. After 30 minutes, dilute the solution 10-fold with 1.0M H_2SO_4, and measure the absorbance at 670 nm.

12.2.6 Calculate the amount of sulfide (µmoles) in the sample from the calibration curve. If the total volume of NaOH in the trap was not used in the analysis, account for the portion tested.

12.3 Ion-selective electrode method

12.3.1 Calibrate the sulfide electrode and meter according to manufacturer's recommendations, using sulfide standards prepared in SAOB reagent 7.6.2 diluted 1:1 with DDIW.

12.3.2 Transfer the contents of each sulfide trap into a 100-mL volumetric flask. Rinse the trap with DDIW, adding the rinses to the volumetric flask. Dilute to volume with DDIW.

12.3.3 Pour contents of volumetric flask into a 150-mL beaker, add a stirring bar and place on stirrer. Begin stirring with minimum agitation to avoid entrainment of air into the solution and minimize oxidation of the sample during the measurement.

12.3.4 Rinse sulfide and reference electrodes into waste container and blot dry with absorbent tissue. Immerse electrodes in sample solution.

12.3.5 Allow electrode response to stabilize (8-10 minutes), then take measurement of sulfide concentration. Depending on the meter used, the reading may be directly in concentration units if the meter is in the concentration mode and a 2-

point calibration has been performed. If the readings are in millivolts, convert millivolts to concentration using the calibration curve obtained from standard solutions.

12.3.6 Calculate the amount of sulfide (µmoles) in the sample.

13. CALCULATION OF AVS CONCENTRATION IN SEDIMENTS

13.1 The sediment dry weight/wet weight ratio (R) must be determined separately. Acid volatile sulfides can be oxidized or altered to non-volatile forms during drying.

13.2 Transfer an aliquot of the sediment to a tared 100-mL tared evaporating dish. Weigh the dish plus the wet sediment. Calculate the wet weight of the sample. Dry the sediment at 104 °C and weigh. Calculate the dry weight of sediment.

13.3 Determine the ratio of dry weight to wet weight for the sediment sample:

$$R = \frac{W_d}{W_w}$$

where R = ratio of dry weight to wet weight,

W_d = dry weight of sediment sample (g), and

W_w = wet weight of sediment sample (g).

Also, the weight of water, W_{water}, taken in a sample for AVS analysis can be calculated. If the weight of the wet sediment sample taken for the AVS analysis is W_{s+w}, the weight of water contained in the sediment sample would be

$$W_{water} = W_{s+w} - (R \times W_{s+w})$$

The volume of water in the sample equals the weight of water, assuming the density is near unity.

13.4 Compute the sulfide concentration per gram dry weight of sediment:

$$AVS\ (\mu moles / g) = \frac{S}{R \times W_w}$$

where S = the amount of AVS in sediment (µmoles) from Section 12.1.4,

12.2.6, or 12.3.6, as appropriate,

R = ratio of dry weight to wet weight from Section 13.3, and

W_w = wet weight of sediment (g) taken for AVS analysis.

13.4 The QC data obtained during the analysis provides an indication of the quality of the sample data and should be provided with the sample results.

14. DETERMINATION OF SIMULTANEOUSLY EXTRACTED METALS (SEM)

14.1 After the generation of sulfide has been completed, filter the sediment suspension remaining in the H_2S generation flask (Section 11.4) through a 0.2 µ membrane filter resistant to attack by acid.

14.2 Transfer the solution to a 250-mL volumetric flask. Rinse the filtering flask with distilled water, adding the rinses to the volumetric flask. Dilute to volume with deionized water.

14.3 Determine the concentrations of cadmium, copper, mercury, nickel and zinc by atomic absorption, inductive coupled plasma spectrometic, or another approved method (7,8). Convert µg/L concentration values to µmoles/L. Multiply the µmoles/L by the solution volume to obtain the µmoles of metal.

14.4 Report the concentrations of each of the metals in the sediment on a µmole per gram dry sediment (µmol/g) basis.

14.5 Calculate the ratio of SEM to AVS:

$$\frac{\text{SEM}}{\text{AVS}} = \frac{\sum[\text{metal}]}{\text{AVS}}$$

where SEM is the sum of the concentrations of metals, Σ [metal], for the metals cadmium, copper, lead, mercury, nickel and zinc in Section 14.4, and

AVS is the acid volatile sulfide concentration determined in Section 13.4.

Both SEM and AVS are expressed on a µmole per gram dry sediment (µmol/g) basis.

14.6 A SEM:AVS ratio greater than one suggests that toxicity is possible while a ratio less than one suggests that the metals in the sediment are not toxic (2).

15. REFERENCES

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