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The Analysis of Chemical Digester Sludges for Metals by Several Laboratory Groups

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THE ANALYSIS OF CHEMICAL DIGESTER SLUDGES FOR METALS BY SEVERAL LABORATORY GROUPS

by

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ABSTRACT

The research program, conducted under the Canada-Ontario Agreement on Great Lakes Water Quality, identified a significant concern for the disposal of municipal sludges produced from the chemical treatment of sewage for phosphorus removal.

As a result, a comprehensive, multi-agency program was established to examine the potential use of sludge as fertilizer and to investigate the risk of sludge becoming an environmental contaminant.

To help verify analytical data collected, an interlaboratory comparison was conducted on four homogenized and dried municipal sludges from sewage treatment plants where chemical treatment was used for phosphorus removal. Constituents of interest were various metallic species. This report presents results obtained on the samples by atomic absorption spectrophotometry following sample pretreatment. The preparation of standards, aspects of sample preparation and problems encountered in the analysis of the samples are discussed. The atomic absorption data is compared to results obtained on the same samples by X-ray fluorescence, activation analyses (neutron and photon) and atomic emission. Finally, the samples are suggested for use as "standards" for analysis of similar materials.

RÉSUMÉ

L'Ontario et le Canada ont entrepris un programme de recherche en vertu de l'accord sur la qualité de l'eau des Grands lacs. Ce programme a montré qu'il faut s'occuper d'éliminer les boues résultat de la déphosphatation par voie chimique des eaux résiduaires issues des installations municipales.

En conséquence, un programme d'ensemble, établi en collaboration avec plusieurs organismes, vise à trouver les moyens convertir ces boues en engrais et à évaluer les risques de contamination du milieu.

Pour mieux vérifier les données analytiques, on a comparé, dans différents laboratoires, quatre échantillons homogénéisés et séchés de ces boues. Les recherches ont porté sur divers éléments métalliques. Les résultats de l'examen par spectrophotométrie d'absorption atomique des échantillons préalablement traités se trouvent dans le présent rapport. Il y est question de l'étalonnage, de la préparation des échantillons et des problèmes rencontrés en cours d'analyse. Les données recueillies par spectrophotométrie d'absorption atomique sont comparées aux résultats obtenus par fluorescence des rayons X, par activation neutronique et photomique et par spectrophotométrie d'emission atomique. Le rapport propose en outre, d'utiliser les échantillons comme étalons dans l'analyse de substances semblables.

TABLE OF CONTENTS

LIST OF TABLES

1 INTRODUCTION

On August 13, 1971, the Canada-Ontario Agreement on Great Lakes Water Quality was signed. The purpose of this Agreement was to permit the Government of Canada to carry out its obligations under the Canada-U.S. Agreement which was signed subsequently on April 15, 1972. The Canada/Ontario Agreement provided for the acceleration of the construction of municipal sewage treatment facilities and the introduction of phosphorus removal at all significant municipal sources. In addition, several broad areas of research activity were defined under this Agreement, one of which was chemical treatment using existing municipal treatment systems. This led to the study of the removal of phosphorus from sewage using either lime, various iron salts or alum as precipitants (LeClair, 1973). During this treatment process, the calcium, iron or aluminum becomes incorporated into the sludges as do other metals which are initially present in the raw sewage (Cheung et al, 1973). The large sludge volume which is generated, the possibility that this material could prove useful as a fertilizer in agricultural applications, the saving in money which could be realized using land disposal methods, and the recognition of potential environmental problems which might result when crops are grown on these sludges led to the development of a comprehensive program on the subject of disposal of sewage sludges on agricultural land. A number of these studies were carried out at the Wastewater Technology Centre (Bryant et al, 1977 and Chawla et al, 1977). Field and greenhouse studies were conducted by the University of Guelph (Bates et al, 1977).

Because there were several groups involved in the program, a means of verification of analytical results was necessary and, although some materials exist which could be used as standards for some elements (e.g., National Bureau of Standards, orchard leaves, bovine liver, tomato leaves), no totally satisfactory reference standards were available for use in sludge analysis. A potentially good way of verifying results and checking the accuracy of analytical procedures is the exchange of samples between laboratories. It was decided, therefore, to initiate a comparative analytical study involving various interested agencies, in particular, the University of Guelph, University of Toronto, Soil Research Institute of Agriculture Canada (Ottawa), and the Ontario Ministry of the Environment (Toronto), in the hope of identifying any problem areas in the analysis of metallic constituents in sludge. Interest in the study grew quickly. Twenty-five laboratories have participated thus far.

The analysis of four dried sludge samples for 14 elements is reported and discussed in this report. Data are also presented on the use of these samples as long-term "in-house" standards.

2 STUDY OBJECTIVES

The main objectives of this study were the comparison of analytical results obtained from various interested laboratories and statistical evaluation of these results to verify the data collected in the sludge utilization programs.

3 EXPERIMENTAL PROGRAM

Samples of sludge were collected separately from the digesters of four sewage treatment plants in Ontario - namely Newmarket, North Toronto, Sarnia, and Point Edward. The sludges designated A, B, D, and F, respectively, for the purposes of this program, were from phosphorus removal treatment processes involving additions of lime (A), ferric chloride (B and D) and ferric chloride plus lime (F).

A 45-gallon quantity of each sample was thoroughly mixed using mechanical stirrers to promote homogeneity and to assist the breaking up of any lumps. After four or five days of this treatment, a portion of the wet sludge was removed and allowed to air-dry for three to four days. The dry material was ground using a soil grinder (Model 4E, Straub Co., Croydon, Pennsylvania) followed by a Wiley mill (Arthur H. Thomas Co.) equipped with a 60 mesh screen.

Each bulk sample was then divided and packaged in small vials (approximately 10 grams) for distribution. As a check of homogeneity, the content of each vial was sampled and analyzed for selected metals using flame atomic absorption. The digestion employed for sample preparation before analysis was an aqua regia hydrogen peroxide digestion as outlined in Analytical Methods Manual, Wastewater Technology Centre, June, 1976 (unpublished).

4 METHODS OF ANALYSIS

Most laboratories used flame atomic absorption following various methods of sample preparation. The methods of sample preparation included aqua regia (Van Loon and Lichwa, 1973), sulphuric acid and nitric and perchloric acids, in various combinations. Other methods of sample preparation used were the Parr digestion bomb (Agemian and Chau, 1975) and a lithium metaborate fusion in graphite crucibles (Van Loon and Parissis, 1969). Other instrumental methods of analysis used were:

(i) flame emission spectrophotometry;
(ii) X-ray fluorescence;
(iii) nuclear activation analysis (see also Perek, 1974 and Chattopadhyay, 1976); and
(iv) cold vapor atomic absorption analysis (mercury only).

As well as being evaluated by nuclear activation analysis, mercury analysis was performed using cold vapor atomic absorption (Hatch and Ott, 1968) by six laboratory groups. In all cases where cold vapor atomic absorption was used, an oxidizing digestion was employed to convert all the mercury to the oxidized (+2) form. The mercury was then chemically reduced to the elemental state and measured using cold vapor atomic absorption spectrophotometry.

5 EVALUATION OF DATA

All values reported for each parameter were used in the statistical evaluation. A few laboratories used more than one method for some parameters. In these cases, each result was considered as a separate value. After rejection of outliers by the method of Grubbs (1969) at the 5% significance level (indicated by an R in the tables) the mean, standard deviation and relative standard deviation (RSD) were calculated for each parameter. Relative standard deviation is a measure of precision. Results are shown in Tables 6 to 12 and Tables 15 to 21.

The four dried sludge samples (A, B, D, F) were analyzed several times using flame atomic absorption by the Wastewater Technology Centre laboratory. Results of the long term study are presented in Tables 2 to 5.

Table 1 presents briefly all the methods used in the analysis of the four dried sludges; Tables 13 and 14 present information on the use of background correction in connection with atomic absorption analysis of the sludges for cadmium and lead; Table 22 lists the metal concentrations of the four reference sludges based on the findings of this study.

The instrumental methods could not be compared statistically against each other because there was insufficient data.

TABLE 1. OUTLINE OF ANALYTICAL METHODS USED IN THE INTERLABORATORY STUDY

All analysis based on an aqua regia digestion followed by atomic absorption measurement except:

a	atomic absorption after perchloric acid type digestion;
b	atomic absorption after sulphuric-nitric digestion;
c	atomic absorption after lithium metaborate fusion;
d	atomic absorption after hydrochloric acid digestion;
e	atomic absorption after nitric acid digestion;
f	atomic absorption after perchloric, hydrofluoric, peroxide type digestion;
g	atomic absorption after perchloric, hydrofluoric, sulphuric type digestion;
h	flame emission after hydrochloric leach on ignited sample, brought to dryness then leached with boiling distilled water;
i	flame emission spectroscopy after hydrochloric leach;
j	flame emission spectroscopy after aqua regia digestion;
k	cold vapor atomic absorption;
m	X-ray fluoresence; and
n	activation (neutron-photon) analysis.

Note: R-value rejected (method of Grubbs, 1969).

TABLE 2. ANALYSIS OF SAMPLE A† BY ONE LABORATORY††

Element	Mean	Standard Deviation	RSD (%)	Number of Determinations
Zinc	735	42.3	5.8	10
Copper	153	9.31	6.1	10
Chromium	26.3	2.09	7.9	11
Nickel	7.36	1.69	22.9	10
Lead*	136	7.92	5.8	9
Lead**	101	1.72	1.7	5
Cadmium*	5.95	2.07	34.8	4
Cadmium**	2.05	0.446	24.4	7
Manganese	242	16.0	6.6	11
Iron (%)	0.60	0.061	10.0	11
Aluminum (%)	0.21	0.013	6.1	11
Calcium (%)	27.3	1.77	6.5	11
Magnesium (%)	0.29	0.035	11.8	11
Sodium	418	79.7	19.1	11
Potassium	439	49.8	11.1	10

All means and standard deviations in µg/g except where indicated.
* Not background corrected.
** Background corrected.
† Samples described in Section 3.
†† Wastewater Technology Centre laboratory.

TABLE 3. ANALYSIS OF SAMPLE B† BY ONE LABORATORY††

Element	Mean	Standard Deviation	RSD (%)	Number of Determinations
Zinc	2650	120	4.5	11
Copper	1330	91.2	6.9	11
Chromium	391	42.8	10.9	11
Nickel	27.8	3.93	14.1	10
Lead*	1082	20.8	1.9	5
Lead**	1040	81.1	7.8	6
Cadmium*	20.4	1.88	9.2	4
Cadmium**	18.7	1.78	9.5	7
Manganese	399	29.7	7.4	11
Iron (%)	7.65	0.676	8.8	11
Aluminum (%)	1.75	0.200	11.4	11
Calcium (%)	4.53	0.466	10.3	11
Magnesium (%)	0.64	0.098	15.1	9
Sodium	1730	349	20.1	11
Potassium	2010	339	16.9	11

All means and standard deviations in µg/g except where indicated.
* Not background corrected.
** Background corrected.
† Samples described in Section 3.
†† Wastewater Technology Centre laboratory.

TABLE 4. ANALYSIS OF SAMPLE D† BY ONE LABORATORY††

Element	Mean	Standard Deviation	RSD (%)	Number of Determinations
Zinc	10400	883	8.5	11
Copper	776	67.2	8.7	11
Chromium	163	6.75	4.1	10
Nickel	32.7	3.56	10.9	11
Lead*	3350	166	5.0	9
Lead**	3090	193	6.2	6
Cadmium*	88.6	4.12	4.7	4
Cadmium**	90.2	2.25	2.5	7
Manganese	2490	247	9.9	11
Iron (%)	9.85	0.871	8.8	11
Aluminum (%)	1.07	0.162	15.1	11
Calcium (%)	4.94	0.538	10.9	11
Magnesium (%)	0.934	0.096	10.3	10
Sodium	688	154	22.3	11
Potassium	1380	236	17.1	11

All means and standard deviations in µg/g except where indicated.
* Not background corrected.
** Background corrected.
† Samples described in Section 3.
†† Wastewater Technology Centre laboratory.

TABLE 5. ANALYSIS OF SAMPLE F† BY ONE LABORATORY††

Element	Mean	Standard Deviation	RSD (%)	Number of Determinations
Zinc	927	120	12.9	11
Copper	653	43.7	6.7	11
Chromium	115	5.59	4.9	10
Nickel	20.7	2.42	11.7	11
Lead*	588	18.9	3.2	8
Lead**	557	29.1	5.2	5
Cadmium*	7.75	1.66	21.4	4
Cadmium**	5.29	1.29	24.4	7
Manganese	407	26.1	6.4	11
Iron (%)	6.32	0.621	9.8	11
Aluminum (%)	1.41	0.202	14.3	10
Calcium (%)	13.3	1.30	9.8	11
Magnesium (%)	0.554	0.039	7.1	10
Sodium	894	205	22.9	11
Potassium	577	131	22.7	11

All means and standard deviations in µg/g except where indicated.
* Not background corrected.
** Background corrected.
† Samples described in Section 3.
†† Wastewater Technology Centre laboratory.

TABLE 6. SUMMARY OF ZINC RESULTS (μg/g)

Sample #	A	B	D	F
Lab #				
1	662	2640	8790	670
2	730^a	2830^a	4910^{a}R	920^a
3	730;800^a	2500;2870^a	10200	884
4	700	2200	10000	800
5	790	2610	10600	900
6	750	2470	9800	857
7	820;750^m	2890;2720^m	9800;10100^m	800;900^m
8	735	2650	10400	927
9	700;690^d	2250;2500^d	8600	720
14	563^n	2661^n	9700^n	780^n
18	820^a;810^b	2700^a;2500^b	12125^a;11500^b	915^a;750^b
20	600^b	1400^{b}R	6000^b	880^b
$\bar{x}$	737	2588	10160	846
Standard Deviation	63.1	202	979	83.7
RSD (%)	8.6	7.8	9.6	10.0
n	15	15	12	14

Notes:
1. Superscripts identified in Table 1.
2. R-value rejected (method of Grubbs, 1969).
3. Samples described in Section 3.

TABLE 7. SUMMARY OF COPPER RESULTS (μg/g)

Sample #	A	B	D	F
Lab #				
1	160	1330	710^a	580^a
2	173^a	1426^a	744^a	625^a
3	155;140^a	1500;1000^a	849	736
4	150	1200	810	640
5	159	1430	800	618
6	165	1410	848	733
7	183;110^mR	1530;1280^m	900;800^m	900;800^m
8	153	1330	776	653
9	150;150^d	1310;1380^d	1320R	640
14	-	-	-	-
18	185^a;185^b	1400^a;1220^b	835^a;820^b	715^a;585^b
20	160^b	1060^b	630^bR	520^b
$\tilde{x}$	162	1321	808	672
Standard Deviation	14.4	149	52.4	102
RSD (%)	8.9	11.3	6.5	15.2
n	14	15	11	13

Notes:
1. Superscripts identified in Table 1.
2. R-value rejected (method of Grubbs, 1969).
3. Samples described in Section 3.

TABLE 8. SUMMARY OF MANGANESE RESULTS (µg/g)

Sample #	A	B	D	F
Lab #				
1	275	410	2600^{a}	430^{a}
2	271^{a}	434^{a}	2540^{a}	4080^{a}R
3	252;282^{a}	352;308^{a}	2950	470
4	220	370	2200	400
5	250	431	2700	400
6	286	448	2620	414
7	240	375	2400;2800^{m}	400;400^{m}
8	242	399	2490	407
9	-	-	2600	440
14	235^{n}	400^{n}	2400^{n}	400^{n}
18	-	-	-	-
20	210^{b}	370^{b}	2300^{b}	340^{b}
$\bar{x}$	251.2	391	2550	409.2
Standard Deviation	25.0	40.9	210.8	32.1
RSD (%)	10.0	10.5	8.3	7.8
n	11	11	12	11

Notes:
1. Superscripts identified in Table 1.
2. R-value rejected (method of Grubbs, 1969).
3. Samples described in Section 3.

TABLE 9. SUMMARY OF IRON RESULTS (% by weight)

Sample #	A	B	D	F
Lab #				
1	0.63	9.66	8.71^a	5.79^a
2	0.75^a	7.58^a	10.8^a	6.44^a
3	0.54;0.64^a	6.18;7.16^a	9.3	5.5
4	0.5	7	9.3	5.6
5	0.60	7.5	9.46	6.85
6	0.55	6.87	9.34	6.47
7	0.56	7.20	9.30^m	6.00^m
8	0.60	7.65	9.85	6.32
9	0.23R;0.75^d	5.0;10.0^d	8.20	5.50
14	0.591^n	7.55^n	9.75^n	6.5^n
18	2.2^aR;2.4^bR	7.8^a;8.2^b	7.8^a;8.6^b	8.0^a;8.2^b
20	0.60^b	5.0^b	7.0^b	6.5^b
$\bar{x}$	0.609	7.36	9.03	6.44
Standard Deviation	0.076	1.37	0.98	0.86
RSD (%)	12.5	18.6	10.9	13.4
n	12	15	13	13

Notes:
1. Superscripts identified in Table 1.
2. R-value rejected (method of Grubbs, 1969).
3. Samples described in Section 3.

TABLE 10. SUMMARY OF NICKEL RESULTS (μg/g)

Sample #	A	B	D	F
Lab #				
1	11.3	21.9	44;91[a]	28;66[a]
2	-	-	-	-
3	27;30[a]	38;36[a]	38	22
4	6	28	35	24
5	20	32	35	25
6	24.1	38.0	47.2	34.4
7	6;5[m]	34;16[m]	33	26
8	7.4	27.8	32.7	20.7
9	40;30[d]	30;40[d]	20	10
14	7.3[n]	25.6[n]	30.2[n]	19.5[n]
18	80[a]R;30[b]	65[a];65[b]	85[a];80[b]	80[a];60[b]
20	5[b]	7[b]	20[b]	7[b]
$\bar{x}$	17.8	33.6	45.5	32.5
Standard Deviation	12.2	15.5	24.1	22.2
RSD (%)	68.5	46.1	52.9	68.3
n	14	15	13	13

Notes:
1. Superscripts identified in Table 1.
2. R-value rejected (method of Grubbs, 1969).
3. Samples described in Section 3.

TABLE 11. SUMMARY OF CADMIUM RESULTS (μg/g)

Sample #	A	B	D	F
Lab #				
1	7.6	27.2	126^{a}R	11.0^{a}
2	-	-	-	-
3	4.5;4.5^{a}	17.5;18.0^{a}	97	5
4	1	14	83	6
5	5.8	20.5	103	5.6
6	6.3	20.9	95.8	8.9
7	2.4;2.0^{m}	18.3;13^{m}	88;80^{m}	10;10^{m}
8	2.1	18.7	90.2	5.3
9	2.5	12	105	13
14	2.0^{n}	16.5^{n}	88.7^{n}	5.0^{n}
18	4^{a};2^{b}	19^{a};6^{b}	82^{a};29^{b}R	7^{a};3^{b}
20	5^{b}	20^{b}	80^{b}	10^{b}
$\bar{x}$	3.69	17.3	90.2	7.68
Standard Deviation	1.98	4.97	8.91	2.98
RSD (%)	53.7	28.7	9.9	38.8
n	14	14	11	13

Notes:
1. Superscripts identified in Table 1.
2. R-value rejected (method of Grubbs, 1969).
3. Samples described in Section 3.

TABLE 12. SUMMARY OF LEAD RESULTS (μg/g)

Sample #	A	B	D	F
Lab #				
1	152	1040	2950^a	650^a
2	-	-	-	-
3	148;140^a	1230;1240^a	3442	626
4	90	980	3100	580
5	135	1250	3220	566
6	132	1130	2980	555
7	104;85^m	1250;1100^m	3300;3300^m	600;600^m
8	101	1040	3090	557
9	150;110^d	1200	3400	640
14	100^n	1000^n	3100^n	565^n
18	160^a;160^b	870^a;495^bR	1740^aR;900^bR	570^a;230^bR
20	140^e	1000^e	3000^e	500^e
$\bar{x}$	127.1	1102	3171	584
Standard Deviation	26.1	125	171.1	41.9
RSD (%)	20.6	11.3	5.4	7.2
n	15	13	11	12

Notes:
1. Superscripts identified in Table 1.
2. R-value rejected (method of Grubbs, 1969).
3. Samples described in Section 3.

TABLE 13. EFFECT OF BACKGROUND CORRECTION ON CADMIUM DETERMINATIONS BY AAS

Sample No.†	Without Correction	With Correction
A	5.95 ppm	2.05 ppm
B	20.4 ppm	18.7 ppm
D	88.6 ppm	90.2 ppm
F	7.75 ppm	5.29 ppm

† Samples described in Section 3.

TABLE 14. EFFECT OF BACKGROUND CORRECTION ON LEAD DETERMINATIONS BY AAS

Sample No.†	Without Correction	With Correction
A	136 ppm	101 ppm
B	1082 ppm	1042 ppm
D	3350 ppm	3090 ppm
F	588 ppm	557 ppm

† Samples described in Section 3.

TABLE 15. SUMMARY OF ALUMINUM RESULTS (% by weight)

Sample #	A	B	D	F
Lab #				
1	0.40	2.17	2.23^a	160^a
2	-	-	-	-
3	-	-	1.32	1.94
4	0.3	1.6	1.1	1.7
5	0.28	2.00	0.97	1.37
6	0.37^c	2.00^c	0.81	1.27
7	-	-	-	-
8	0.21	1.75	1.07	1.50
9	-	0.12R	1.56	1.78
14	-	-	-	-
18	-	-	-	-
20	0.35^b	2.25^b	2.00^b	1.82^b
$\bar{x}$	0.318	1.96	1.38	1.62
Standard Deviation	0.069	0.247	0.509	0.231
RSD (%)	21.6	12.6	36.9	14.3
n	6	6	8	8

Notes:
1. Superscripts identified in Table 1.
2. R-value rejected (method of Grubbs, 1969).
3. Samples described in Section 3.

TABLE 16. SUMMARY OF CHROMIUM RESULTS (μg/g)

Sample #	A	B	D	F
Lab #				
1	37.8	337	194^a	139^a
2	-	-	-	-
3	18.0;33.3^a	575;555^a	170	119
4	23	350	120	95
5	25.0	281	114	80
6	24.1	400	149	140
7	30^m	310^m	140	100
8	26.3	391	159	113
9	20;20^d	300;300^d	142	104
14	27^n	390^n	165^n	110^n
18	20^a;15^b	375^a;185^bR	81^a;90^b	95^a;64^b
20	40^b	300^b	130^b	90^b
$\bar{x}$	25.7	381.6	139	101.3
Standard Deviation	7.39	89.5	33.0	19.2
RSD (%)	28.8	23.5	23.9	19.0
n	14	13	12	12

Notes. 1. Superscripts identified in Table 1.
2. R-value rejected (method of Grubbs, 1969).
3. Samples described in Section 3.

TABLE 17. SUMMARY OF CALCIUM RESULTS (% by weight)

Sample #	A	B	D	F
Lab #				
1	24.2	3.69	2.16[a]	5.88[a]
2	14.9[g]R	4.80[g]	2.58[g]	8.54[g]
3	24.6;26.2[f]	4.5;4.0[f]	4.6	12.2
4	-	-	-	-
5	31.2	5.00	4.40	11.8
6	24.1	4.11	3.44	9.82
7	-	-	-	-
8	27.2	4.54	4.94	13.3
9	-	-	0.38[j]R	0.52[j]R
14	26.8[n]	4.50[n]	4.85[n]	12.8[n]
18	-	-	-	-
20	22.0[d]	4.5[d]	4.5[d]	12.5[d]
$\bar{x}$	25.8	4.40	4.03	11.2
Standard Deviation	2.77	0.405	1.19	3.05
RSD (%)	10.7	9.2	29.5	27.2
n	8	9	8	8

Notes:
1. Superscripts identified in Table 1.
2. R-value rejected (method of Grubbs, 1969).
3. Samples described in Section 3.

TABLE 18. SUMMARY OF MAGNESIUM RESULTS (μg/g)

Sample #	A	B	D	F
Lab #				
1	2600	3370	10800^a	5600^a
2	3740^a	8260^a	13300^a	7500^aR
3	$303;410^a$	$778;808^a$	11400	6200
4	-	-	-	-
5	2300	5600	11200	6500
6	3280	8290	9700	5700
7	-	-	-	-
8	2940	6280	9340	5540
9	-	-	9450	5100
14	3010^n	6000^n	9000^n	5000^n
18	-	-	-	-
20	2200^d	6100^d	9100^d	5600^d
$\bar{x}$	2309	5054	10370	5655
Standard Deviation	1205	2822	1430	502.8
RSD (%)	52.2	55.8	13.8	8.9
n	9	9	9	8

Notes:
1. Superscripts identified in Table 1.
2. R-value rejected (method of Grubbs, 1969).
3. Samples described in Section 3.

TABLE 19. SUMMARY OF SODIUM RESULTS (μg/g)

Sample #	A	B	D	F
Lab #				
1	-	-	1400^{a}R	3300^{a}R
2	-	-	-	-
3	-	-	-	-
4	-	-	-	-
5	700	4600	605	1030
6	548^{h}	1580^{h}	700^{h}	1250^{h}
7	-	-	-	-
8	418	1730	688	894
9	4800^{i}R; 2400^{j}R	2200^{i}; 2400^{j}	880^{j}R	1360^{j}
14	420^{n}	1700^{n}	650^{n}	900^{n}
18	-	-	-	-
20	250^{j}	1900^{j}	600^{j}	850^{j}
$\bar{x}$	474	2016	649	1047
Standard Deviation	173	389	46.0	211
RSD (%)	36.5	19.3	7.1	20.1
n	5	7	5	6

Notes: 1. Superscripts identified in Table 1.
2. R-value rejected (method of Grubbs, 1969).
3. Samples described in Section 3.

TABLE 20. SUMMARY OF POTASSIUM RESULTS (μg/g)

Sample #	A	B	D	F
Lab #				
1	-	-	800[a]	1000[a]
2	2500[g]	5140[g]	6140[g]R	1970[g]R
3	520;2750[f]	2640;5200[f]	1510	707
4	-	-	-	-
5	750	2400	1330	537
6	382[h]	2170[h]	1870[h]	850[h]
7	-	-	-	-
8	467	2010	1380	577
9	-	-	2600	920
14	-	-	-	-
18	-	-	-	-
20	300[d]	1700[d]	800[d]	400[d]
$\bar{x}$	1095	3037	1470	713
Standard Deviation	1057	1487	628	220
RSD (%)	96.5	48.9	42.7	30.9
n	7	7	7	7

Notes: 1. Superscripts identified in Table 1.
2. R-value rejected (method of Grubbs, 1969).
3. Samples described in Section 3.

TABLE 21. SUMMARY OF MERCURY RESULTS (µg/g)

Sample #	A	B	D	F
Lab #				
1	-	-	8.4^{k}	2.2^{k}
2	-	-	-	-
3	-	-	-	-
4	-	-	10^{k}	1^{k}
5	-	-	9.08^{k}	2.5^{k}
6	-	-	8.17^{k}	1.86^{k}
7	2.4^{k}	28^{k}	7.7^{k}	1.0^{k}
8	-	-	-	-
9	-	-	-	-
14	2.2^{n}	25^{n}	8.0^{n}	1.42^{n}
18	-	-	-	-
20	0.2^{k}R	3.1^{k}R	1.6^{k}R	0.2^{k}
$\bar{x}$	2.3	26.5	8.56	1.45
Standard Deviation	0.14	2.12	0.846	0.79
RSD (%)	6.1	8.0	9.9	54.9
n	2	2	6	7

<u>Notes</u>: 1. Superscripts identified in Table 1.
2. R-value rejected (method of Grubbs, 1969).
3. Samples described in Section 3.

TABLE 22. METAL CONCENTRATIONS* IN REFERENCE SLUDGE SAMPLES

Element**	Sample			
	A	B	D	F
Calcium	27.3 ± 1.7†	4.53 ± 0.47†	4.94 ± 0.54†	13.3 ± 1.3†
Magnesium	0.29 ± 0.03†	0.64 ± 0.10†	0.93 ± 0.09†	0.55 ± 0.04†
Iron	0.61 ± 0.06†	7.65 ± 1.37†	9.85 ± 0.87†	6.32 ± 0.62†
Aluminum††	0.21 ± 0.01†	1.75 ± 0.20†	1.07 ± 0.16†	1.41 ± 0.20†
Zinc	735 ± 42	0.27 ± 0.01†	1.04 ± 0.09†	927 ± 120
Copper	153 ± 9	0.13 ± 0.01†	776 ± 67	653 ± 44
Nickel	7.4 ± 1.7	27.8 ± 3.9	32.7 ± 3.6	20.7 ± 2.4
Lead	101 ± 2	0.10 ± 0.01†	0.31 ± 0.02†	557 ± 29
Cadmium	2.1 ± 0.4	18.7 ± 1.8	90.2 ± 2.3	5.3 ± 1.3
Manganese	242 ± 16	339 ± 30	0.25 ± 0.03†	407 ± 26
Chromium	26.3 ± 2.1	391 ± 43	163 ± 7	115 ± 6
Sodium	418 ± 80	0.17 ± 0.04†	688 ± 150	894 ± 200
Potassium	439 ± 50	0.20 ± 0.03†	0.14 ± 0.02†	577 ± 130
Mercury	2.3	26.5	8.56 ± 0.85	1.66 ± 0.63

All values expressed in µg/g except where indicated.
* Including standard deviation of Samples A, B, D and F.
** Samples described in Section 3.
† Values and standard deviation expressed in (% by weight).
†† Analysis defined as acid leachable.

6 DISCUSSION OF RESULTS

6.1 Zinc, Copper, Manganese and Iron

As evidenced by the low relative standard deviations, the analysis of these four constituents presented minimum difficulty. The quantities present were high enough to permit direct measurement after proper sample preparation. It was found that the intralaboratory precision (Tables 2 to 5) was better than interlaboratory precision with these four elements (Tables 6 to 9). This was expected because of the variety of analytical techniques used (Tables 6, 7, 8 and 9).

6.2 Nickel, Cadmium and Lead

With all three elements, the intralaboratory precision was well below the interlaboratory precision. On examining the reported results for nickel determinations by atomic absorption methods, it is evident that they fall into two categories - those in which some form of background correction was used and those in which background correction was not used. This division is particularly noticeable with sample A (high calcium). Four results were calculated using background correction (6.1 ppm), eight did not use background correction (26.5 ppm), and one value was rejected (Tables 10, 11 and 12).

Nonspecific absorbance was evident in some of the other samples. For example, in sample D, one particular laboratory not using background correction, performed two different digestions - one using hydrofluoric acid, nitric acid, and perchloric acid in a Parr digestion bomb and a second digestion using aqua regia in glass beakers. The results for nickel determinations were 91 ppm and 44 ppm, respectively. The higher value (91 ppm) was probably due to the higher acid content in the extract. This problem has been discussed previously (Knechtel and Fraser, 1974).

In the analysis of cadmium by atomic absorption, differences in reported results can probably be attributed to nonspecific absorbance. At the Wastewater Technology Centre these four samples were analyzed with and without background correction (deuterium arc) and the values are shown in Table 13.

Also with cadmium, the interlaboratory variation (Table 11) was not as good as the intralaboratory precision (Tables 2 to 5). This was probably caused by both the variety of techniques used and the cadmium level in the samples.

The precision in the analysis of lead was less than 11% in the case of interlaboratory variation with sample A. It is likely here that the high calcium content caused nonspecific absorbance problems in atomic absorption analysis. At the Wastewater Technology Centre these samples were analyzed with and without background correction. The values are shown in Table 14.

The three values rejected in Table 12 were obtained using atomic absorption following a sulphuric-nitric digestion. The reason these results were low is probably due to the precipitation of lead as lead sulphate.

6.3 Aluminum

The only instrumental technique employed in the evaluation of aluminum was atomic absorption. It is evident from Table 15 that sample preparation techniques had a significant bearing on the aluminum results with some samples. With samples B and F differences in values obtained cannot be attributed to sample preparation techniques. With samples A and D, however, there was a large spread in the values obtained by aqua regia type preparations. With these two samples also, fusions, digestions with hydrofluoric acid, and sulphuric-nitric digestions gave higher values than did aqua regia preparations.

6.4 Chromium

In the data presented for the analysis of chromium, the interlaboratory precision (Table 16) was not as good as the intralaboratory precision (Tables 2 to 5) with all four samples. This was probably caused by differences in gas mixtures used in the actual determination. Some laboratories used air-acetylene, whereas others used nitrous oxide-acetylene.

6.5 Calcium

As in the case of lead, some of the variation in reported results can be attributed to the use of unsuitable preparation techniques. The use of sulphuric acid and hydrofluoric acids by some laboratories probably produced insoluble precipitates and hence low values. One laboratory which analyzed by flame emission spectrophotometry obtained an extremely low value for calcium on two of the samples. The strong depression of the calcium emission (and other alkaline earth elements) under conditions such as these has been known for some time (Willard et al, 1965). (Table 17.)

6.6 Magnesium

Two of the four samples gave relative standard deviations greater than 50%. These high figures were caused by low results sent by one laboratory which did not follow the accepted practice of adding lanthanum to the acid extracts before analysis (Table 18).

6.7 Sodium and Potassium

The analytical results for sodium and potassium are shown in Tables 19 and 20. Two general observations were made:

1. Generally analysis based on standards which contain a high concentration of an alternate univalent ion yielded lower values than those not containing a high concentration of an alternate univalent ion.
2. In one instance, a very mild acid leach yielded lower results than regular digestion.

The reason for the high readings obtained in the samples not containing a high concentration of an alternate univalent ion is probably related to the phenomenon of flame ionization. This type of interference is discussed at length elsewhere (Basic Atomic Absorption - Varion Techtron, Pty., 1975) In practice, this type of interference can be effectively avoided by "buffering" the standard with a high concentration of ions of an easily ionizable element. Provided that the concentration of the ion chosen is much greater than the analyte element and its ionization potential is lower or nearly the same as the analyte element, essentially complete suppression of flame ionization may be effected.

The lower results obtained for sodium after the mild acid leach are to be expected because of the strong likelihood that some type of semi-refractory sodium compound was present.

6.8 Mercury

All values for mercury determinations were comparable with the noted exception of those from laboratory 20. Since this laboratory is the only one which did not use some heat in the sample preparation phase of analysis, it would appear that heating the sample during preparation leads to higher total mercury values (Table 21).

7 SUMMARY

As a result of this interlaboratory study, observations and experiences concerning sludge sample preparation and instrumental techniques to be used for the analysis of chemical digester sludges for metals can be summarized as follows:

1. Sample Preparation

(a) Atomic Absorption Analysis. On the basis of this study, the following sample preparation methods, with the qualifications noted, would appear to be satisfactory for this type of sample:

- (i) aqua regia (Van Loon and Lichwa, 1973) - all elements studied except mercury;
- (ii) aqua regia and hydrogen peroxide (Analytical Methods Manual, Wastewater Technology Centre, unpublished) - all elements studied except mercury;
- (iii) nitric acid and perchloric acid digestion - all elements studied except mercury;
- (iv) lithium metaborate fusion (Van Loon and Parissis, 1969) - total aluminum only;
- (v) hydrochloric acid digestion - total calcium, magnesium only;
- (vi) nitric acid digestion - total lead only;
- (vii) digestion including hydrofluoric acid - total aluminum only; and
- (viii) sulphuric acid - nitric acid digestions - total aluminum only.

(b) Flame Emission Analysis. Digest the ignited sludge in hydrochloric acid, take to dryness and then boil in distilled water; filter sample before sodium and potassium analysis.

(c) Cold Vapor Atomic Absorption Analysis. This concerns mercury analysis. Some heat is necessary when preparing samples for mercury analysis.

2. Instrumental Techniques

(a) Atomic Absorption

(i) Background correction is required in the determination of nickel, cadmium and lead, particularly in the evaluation of sludges which are high in calcium.

(ii) In the analysis for sodium and potassium, it is essential that standards used for calibration contain 1000 to 2000 µg/mℓ of another alkali salt. This will prevent flame ionization in the standard which results in an erroneously high reading for the sample being measured.

(iii) In the atomic absorption evaluation of the elements studied with the exception of sodium, potassium and mercury, "mixed standards" should be used for the instrument calibration. These standards should contain several elements (Al, Ba, Ca, Co, Cd, Cr, Fe, Mn, Mg, Mo, Na, K, Si, Ni, Zn, Pb) and the same concentration of the acids which were used in sample preparation.

(b) Neutron and Photon Activation Analysis. The values obtained using activation analysis agreed very well with those measured using conventional flame atomic absorption techniques.

(c) X-Ray Fluorescence. Excellent comparisons with atomic absorption measurements were obtained for the elements evaluated by X-ray fluorescence with the exception of copper in samples containing high levels of calcium.

(d) Cold Vapor Atomic Absorption. (Mercury analysis only.) Excellent comparisons between cold vapor atomic absorption and neutron activation analysis were obtained.

(e) Flame Emission Analysis. (Sodium and potassium only.) The comparisons between atomic absorption and flame emission for sodium analysis were very good. There were insufficient data to draw any comparisons regarding potassium.

8 CONCLUSIONS

It can be concluded that this type of study can serve an extremely useful purpose not only in allowing assessment of laboratory expertise, but also in providing tentative standard values.

These samples are now used on a regular basis for internal checking of sample preparation and analysis at the Wastewater Technology Centre for the elements and values quoted in Table 22.

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