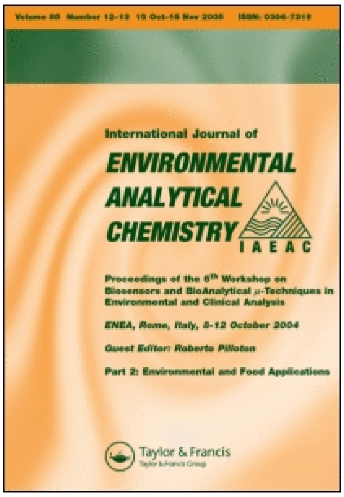

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Comparison of Sample Preparation Methods for the Determination of Metals in Sewage Sludges by Flame Atomic Absorption Spectrometry

S. A. Katz[a]; S. W. Jenniss[b]; T. Mount[c]; R. E. Tout[d]; A. Chatt[d]
[a] Department of Chemistry, Rutgers University, Camden, New Jersey, U.S.A. [b] New Jersey Department of Environmental Protection, Trenton, N.J., U.S.A. [c] Pennsauken Sewage Authority, Pennsauken, N.J., U.S.A. [d] Trace Analysis Research Centre, Dalhousie University, hali, Nova Scotia, Canada

To cite this Article Katz, S. A. , Jenniss, S. W. , Mount, T. , Tout, R. E. and Chatt, A.(1981) 'Comparison of Sample Preparation Methods for the Determination of Metals in Sewage Sludges by Flame Atomic Absorption Spectrometry', International Journal of Environmental Analytical Chemistry, 9: 3, 209 — 220

To link to this Article: DOI: 10.1080/03067318108071515

URL: http://dx.doi.org/10.1080/03067318108071515

Intern. J. Environ. Anal. Chem., 1981, Vol. 9, pp. 209–220
0306-7319/81/0903-0209 $06.50/0

Printed in Great Britain

Comparison of Sample Preparation Methods for the Determination of Metals in Sewage Sludges by Flame Atomic Absorption Spectrometry

S. A. KATZ, S. W. JENNISS† and T. MOUNT‡

Department of Chemistry, Rutgers University, Camden, New Jersey 08102, U.S.A.

and

R. E. TOUT and A. CHATT

Trace Analysis Research Centre, Dalhousie University, Halifax, Nova Scotia, B3H 4J1, Canada

(*Received April 15, 1980; in final form August 25, 1980*)

Sludge samples from the primary settling tank and the first stage digester of a four-million-gallon-per-day sewage treatment plant were prepared for atomic absorption spectrometry by four methods: dry ashing, digestion with nitric acid, digestion with nitric acid and hydrogen peroxide, and digestion with nitric acid in pressure decomposition vessels. The prepared samples were analyzed for cadmium, chromium, copper, iron, lead, nickel and zinc. Typical results were: 50–75 ppm Cd, 15000–20000 ppm Cr, 2500–3000 ppm Cu, 10000–15000 ppm Fe, 3000–3500 ppm Pb, 50–75 ppm Ni and 8000–8300 ppm Zn. In the cases of copper and zinc, these values were confirmed by instrumental neutron activation analysis. In terms of metal recovery, dry ashing appears to be less efficient than digestion with nitric acid in decomposition bombs, digestion with nitric acid and hydrogen peroxide or digestion with nitric acid.

KEY WORDS: Flame atomic absorption, sewage sludge, toxic waste.

---

†New Jersey Department of Environmental Protection, Trenton, N.J., U.S.A.
‡Pennsauken Sewage Authority, Pennsauken, N.J., U.S.A.

INTRODUCTION

At present there are some $8\frac{1}{2}$ million people in New Jersey. Approximately, 75% of this population is sewered and produces 100 g of sewage sludge on a *per capita*, per day basis.[1] The annual sludge production in New Jersey from only domestic sources is in excess of 200,000 metric tons. No firm estimates of the non-domestic contribution to the sludge production are available.

The ultimate fate of sewage sludge is, for the most part, burial in sanitary landfills. Federal regulations have decreased the amount of ocean dumping, and cropland applications of sewage sludge are modest at best. Landfill disposal presents, among other problems, the potential danger of ground water contamination with toxic metals leached from the sewage sludge.[2] On a nation-wide basis, some 50% of the U.S. population is dependent upon ground water for its potable supplies.[3] Hence, the possibility of contamination is of concern. The concern borders on fear in southern New Jersey where potable supply is almost exclusively ground water.[4]

In addition to indicating potential ground water contamination by toxic metals, the elemental analysis of sewage sludge is important in establishing essential and toxic element levels for agricultural and livestock applications. Bastian,[1] and Hinesley, Thomas and Stevens[5] have reviewed the major agricultural applications, and Kienholz *et al.*[6] have used municipal sludge as a dietary supplement for cattle.

While Chattopadhyay[7] has used instrumental neutron and instrumental photon activation analysis for multielement determinations in sewage sludges, atomic absorption spectrometry is most frequently employed to measure the levels of metals in such materials. Prior to making such measurements by atomic absorption spectrometry, however, the sludge samples require proper preparation. There is some controversy over what constitutes proper preparation for the determination of total metal levels in samples of sewage sludge. Hinesley *et al.*[5] express concern in comparing the levels of heavy metals obtained by aqua regia digestion of Bakersfield soils with those obtained from Lubbock soils after dry ashing and digestion with hydrofluoric and hydrochloric acids. Intercomparisons of the values of heavy metals in sewage sludges tabulated by Gurnham and his co-workers[8] should be viewed with the same concern.

A variety of procedures have been employed to prepare sludge samples for atomic absorption spectrometry. Sidel and Kardos[9] digested their samples in a mixture of nitric and perchloric acids. Martin *et al.*[10] have used a mixture of concentrated nitric acid and 30% hydrogen peroxide to digest sludge prior to the measurement of selenium. Sludge samples were dry ashed by Bergman and his co-workers,[11] and the ash was leached with hydrochloric acid prior to the determination of several metals. There are conflicting reports on the efficiency of muffle furnace ignition as a procedure for the preparation of sewage sludge samples.[12,13] While the U.S. EPA[14] recommends, "Treatment plants should analyze their sludges to determine the concentrations of heavy metals", no procedures are specified. Aside from the specific directions for the determination of mercury, the EPA "methods manuals"[15,16] provide little guidance in the analysis of sewage sludges. Kotz *et al.*[17] recommend the following guidelines for sample preparation methods:

1) The decomposition vessels/apparatus should be made from inert materials with high thermal stability and low impurity content to minimize blanks.
2) The decomposition of organic materials must be complete to avoid interferences by organic residues.
3) The decomposition products must be soluble in small volumes of easily purified acids.
4) Adsorption, desorption, volatilization and other sources of systematic error must be eliminated as far as possible.
5) The decomposition method should be simple, rapid and economical.

In the present report, we compare four procedures used to prepare sewage sludge samples for atomic absorption spectrometry.

MATERIALS AND METHODS

Sludge samples were collected from the primary settling tank and from the first stage digester at the Pennsauken Sewage Authority's treatment plant (Pennsauken, N.J.). This plant serves some 40,000 domestic customers and handles 4 million gallons per day of mixed (50/50) industrial–domestic sewage. The solids and ash for these sludges were as follows:

	Total solids (%)	Ash (%)
Primary settling tank sludge	5.2	2.0
First state digester sludge	10.5	3.1

Four procedures were employed to prepare the sludge samples for the determination of cadmium, chromium, copper, iron, nickel, lead and zinc by atomic absorption spectrometry. Chromium, copper, nickel and zinc levels were also determined by instrumental neutron activation analysis. These five approaches to the determination of metals in sewage sludges are outlined below:

Method 1

Instrumental Neutron Activation Analysis: Five 50-mg samples of each of the dried sludges were weighed into plastic irradiation vials and heat sealed. Blanks and multielement standards were similarly prepared. The samples, standards and blanks were irradiated for 10 minutes in a thermal flux of 5.0×10^{11} at the Dalhousie University SLOWPOKE Reactor facility. The irradiated materials were allowed to decay for 1 minute and counted for ^{66}Cu activity using the 1039 keV photopeak. The samples, standards and blanks were then reirradiated for 16 hours in a flux of 5.0×10^{11} and allowed to decay for 3 weeks prior to counting. The levels of chromium, nickel and zinc were determined from the following photopeak activities: ^{51}Cr at 320 keV, ^{58}Co (from (n, p) reaction with ^{58}Ni) at 811 keV and ^{65}Zn at 1115 keV.

Method 2

Decomposition in Acid Digestion Bombs[18] *Followed by Atomic Absorption Spectrometry:* Five 200-mg samples of each of the dried sewage sludges were weighed into the Teflon cups of the digestion bombs, and each, including blanks, were treated with 2.5 ml of redistilled nitric acid. The bombs were closed and placed in a 100° oven overnight. The digested contents were treated with 5 mL of high-purity water, filtered through Whatman No. 42 paper into 50-mL volumetric flasks and brought to volume with high-purity water. Further dilutions of these solutions were made as needed for the atomic absorption spectrometric measurements.

Method 3

Decomposition with Nitric Acid and Hydrogen Peroxide[19] *Followed by Atomic Absorption Spectrometry:* Five 200 mg samples of each of the dried sludges were weighed into 125-mL Erlenmeyer flasks. The flasks containing the sludge samples and empty flasks serving as blanks were treated with 5 mL of redistilled nitric acid and 5 mL of high purity water. The flasks were heated gently until most of the acid was evaporated. After cooling, 5 mL more of redistilled nitric acid was added and the flasks were again heated gently until the volume was reduced to approximately 1 mL. The flasks were again allowed to cool, and they were treated with 1 mL of redistilled nitric acid, 1 mL of high-purity water and 2 mL of 30% hydrogen peroxide. The flasks were alternately heated, cooled and treated with additional 1-mL increments of peroxide until no further changes were apparent in these samples. (This was accomplished with four additional 1-mL increments of peroxide.) The contents of the flasks were treated with 5 mL of high-purity water, filtered through Whatman No. 42 paper into 50-mL volumetric flasks and brought to volume with high-purity water. These solutions were diluted further for measurements of the metals by atomic absorption spectrometry.

Method 4

Digestion with Nitric[16] *Acid Followed by Atomic Absorption Spectrometry:* Five 200-mg samples of each of the dried sludges were weighed into 125-mL Erlenmeyer flasks, treated with 5 mL of redistilled nitric acid and heated gently until the volume was reduced to approximately 1 mL. The flasks containing the samples as well as those included as blanks were cooled, treated with 5 mL of redistilled nitric acid and again heated gently. This process was repeated a total of four times to a point where additional acid produced no apparent changes in the samples. The contents of the flasks were treated with 5 mL of high-purity water, filtered through Whatman No. 42 paper into 50-mL volumetric flasks and brought to volume with high-purity water. Further dilutions of these solutions were made as needed for the atomic absorption spectrometric measurements.

Method 5

Decomposition by Dry Ashing and Solubilization by Leaching Followed by Atomic Absorption Spectrometry: Five 200-mg samples of each of the dried sludges were weighed into zirconium crucibles (#10-15LF, B-J Enterprises, Inc., Albany, OR) and ignited in a Bunsen flame. The charred samples were then placed in a 450° furnace for 2 hours to complete the ignition. The ignited residues were cooled and leached three times with 5 mL of hot, 25% (v/v) redistilled nitric acid in high-purity water. The leachates were filtered through Whatman No. 42 paper into 50-mL volumetric flasks and brought to volume with high-purity water. These solutions were diluted as required for the determination of the metals by atomic absorption spectrometry.

A Perkin–Elmer Model 360 atomic absorption spectrometer was used in accord with the manufacturer's directions for the determination of cadmium, chromium, copper, iron, nickel, lead and zinc in the solutions prepared by the procedures outlined in methods 2 through 5.

RESULTS

The results of the metal determination in the primary settling tank sludge are tabulated in Table I and those for the first stage digester sludge are given in Table II. These values are presented as the mean and standard deviation for the five samples of each sludge. The mean values were compared on the basis of sample preparation methods. In cases where the calculated t values exceeded those expected by chance with a probability of 0.950, the differences in the mean values were considered to be significant. The levels of the elements in the sludges showing such

TABLE I

Levels of selected metals in primary settling tank sludge, mg/kg

	Method				
	1	2	3	4	5
Cd		76.7 ±1.7	74.1 ±1.3	64.7 ±2.2	61.0 ±1.8
Cr	4440 ±140	19300 ±650	20200 ±865	21500 ±575	16400 ±1550
Cu	3190 ±210	3400 ±124	3400 ±115	3120 ±417	2580 ±92
Fe		15100 ±2040	14800 ±353	13900 ±426	10600 ±656
Ni		67.0 ±8.5	75.9 ±7.4	90.6 ±16.7	42.5 ±15.1
Pb		3410 ±71	3220 ±73	2970 ±66	2680 ±124
Zn	8310 ±230	8370 ±316	8540 ±201	8200 ±186	7970 ±85

TABLE II

Levels of selected metals in first stage digester sludge, mg/kg

	Method				
	1	2	3	4	5
Cd		66.3 ±5.9	61.7 ±6.7	57.7 ±1.8	58.7 ±1.7
Cr	3900 ±130	16400 ±360	17100 ±1540	18300 ±146	14900 ±1750
Cu	3170 ±125	2970 ±164	2950 ±105	2850 ±56	2560 ±59
Fe		14800 ±405	14200 ±601	13000 ±231	8850 ±471
Ni		82.7 ±14.8	81.4 ±15.3	77.9 ±9.3	50.5 ±7.0
Pb		3080 ±110	2970 ±122	2760 ±51	2680 ±101
Zn	8700 ±220	8150 ±170	8410 ±303	8300 ±146	8060 ±116

significant differences are identified in Tables III and IV. Because of the poor sensitivities of instrumental neutron activation analysis for cadmium, iron and lead, determination of these elements by this technique was not attempted. The nickel levels in both sludges were found to be below 500 ppm by this technique.

TABLE III

Differences between preparation methods on the apparent levels of selected metals in primary settling tank sludge

	Method				
	1	2	3	4	5
1		Cr	Cr	Cr	Cr, Cu Zn
2	Cr		Cd, Pb	Cd, Cr Ni, Zn	Cd, Cr, Cu Fe, Ni, Pb, Zn
3	Cr	Cd Pb		Cd, Cr Fe Pb, Zn	Cd, Cr, Cu Fe, Ni, Pb, Zn
4	Cr	Cd, Cr Ni, Pb	Cd, Cr Fe Pb, Zn		Cd, Cr, Cu Fe, Ni, Pb
5	Cr, Cu Zn	Cd, Cr, Cu Fe, Ni, Pb, Zn	Cd, Cr, Cu Fe, Ni, Pb, Zn	Cd, Cr, Cu Fe, Ni, Pb	

TABLE IV

Differences between preparation methods on the apparent levels of selected metals in first stage digester sludge

	Method				
	1	2	3	4	5
1		Cr Zn	Cr, Cu	Cr, Cu Pb, Zn	Cr, Cu Pb, Zn
2	Cr Zn			Cd, Cr Fe, Pb	Cd, Cr, Cu Fe, Ni, Pb
3	Cr, Cu			Cr Fe	Cu Fe, Ni Zn
4	Cr, Cu Zn	Cd, Cr Fe, Pb	Cr		Cr, Cu Fe, Ni, Zn
5	Cr, Cu Zn	Cd, Cr, Cu Fe, Ni, Pb	Cu Fe, Ni, Pb, Zn	Cr, Cu Ve, Ni, Zn	

DISCUSSION

The values determined by instrumental neutron activation analysis, INAA, for the chromium levels in the sludges do not agree with those determined by atomic absorption spectrometry, AAS. Behne and Bratter,[20] however, found excellent agreement between INAA results and those obtained by flameless AAS after pressure bomb digestion with nitric acid for the determination of chromium levels in brewers' yeast. They also found chromium levels some 50% lower by flameless AAS after digestion of the brewers' yeast with nitric acid in open beakers. Copper and zinc levels determined by INAA in the primary settling tank sludge agree with those determined by AAS after wet digestion by methods 2, 3 and 4. Dry ashing, on the other hand, gives results lower than those obtained by the other methods. The results for the sludge from the first stage digester also appear to follow this trend.

The results obtained from samples decomposed in the digestion bombs agreed well with those obtained from samples digested with nitric acid and hydrogen peroxide The results obtained by method 2 were, in most cases, higher than those from methods 4 and 5. Although they made no comparisons with other methods, Agemian and Chau[21] found decomposition of lake sediments in acid digestion bombs was an efficient and convenient preparation procedure. Bernas[22,23] has made extensive use of such bombs in decomposing a wide variety of samples. Turnbull,[24] on the basis of several violent explosions in his laboratories, has abandoned the use of pressure bombs. We have experienced only one such explosion in the course of some 700 decompositions. Kotz and his co-workers[17] have substituted vessels fabricated from glassy carbon for the Teflon cups of digestion bombs. The authors cite no instances of explosions even though they carried out their digestions at temperatures some 100° above those commonly used.

The results from the nitric acid–hydrogen peroxide digestion agree with those from the bomb digestions in most cases, but they are higher, for the most part, than those obtained from samples digested with nitric acid alone, method 4, and from samples prepared by dry ashing. Martin *et al.*[10] have used the nitric acid–hydrogen peroxide digestion for the determination of selenium in sludge, and Budna and Knapp[25] have developed a semi-automatic, wet-ashing procedure using sulfuric acid and hydrogen peroxide to digest organic material. Oehme[26] recommends a mixture of nitric, perchloric and sulfuric acids for the digestion of organic materials, but others[13] avoid perchloric acid on the basis of its explosive nature. Ritter and his co-workers[12] found the mixed acids (nitric and perchloric acids) appeared to be more efficient than nitric acid alone in the digestion of sewage sludges for metal determinations. Delfino and Enderson,[13] however, report little difference in the results obtained from solutions prepared by the nitric acid digestion, nitric acid–hydrogen peroxide digestion or nitric acid–hydrochloric acid digestion of sewage sludges.

While the information in Tables III and IV indicate that digestion in nitric acid is less efficient than methods 2 and 3, Schachter and Boyer[27] have reported efficient, safe and rapid digestions of organic materials with nitric acid in a quartz flask with a glass recycling apparatus. Wisseman and Cook[28] have employed a nitric acid reflux to prepare lake sediments for metal determinations, but their work reports no comparisons with other procedures or results on standard materials.

Dry ashing appears to be the least efficient of the sample preparation procedures. Results from the solutions obtained by dry ashing and leaching the ash with nitric acid are significantly lower than those from the other preparation procedures for most metals in both sludge samples. Zirconium crucibles were employed for the ashing to minimize the problems of contamination and absorption attributed to porcelain by Zief and Mitchell.[29] Ritter *et al.*[12] have found dry ashing to be superior to nitric acid and aqua regia digestion of sewage sludges, and they conclude, "The dry ash digestion method is the best for preparing soil and sludge samples for atomic absorption analysis". Hoenig *et al.*[30] have found that wet and dry ashing procedures can be applied successfully for the routine determination of trace elements in plant tissues. The U.S. EPA[31] has considered a procedure for the determination of lead in sludges whereby the samples would be dry ashed for 8 hours at 450° and then refluxed for 2 hours with 50% (v/v) nitric acid prior to atomic absorption spectrometric measurements. Watling and Wardale[32] have compared dry ashing with and without magnesium nitrate to wet ashing with nitric and perchloric acids and with nitric acid and hydrogen peroxide. Significant quantities of lead and cadmium were lost in the course of their dry ashing of tissue samples from marine animals in porcelain crucibles, and nickel and manganese impurities in the magnesium nitrate precluded the use of the magnesium nitrate as an ashing aid. With careful control of the ashing temperatures and with the use of "suprapur" reagent magnesium nitrate, they obtained results by dry ashing approaching those obtained by the wet ashing procedures. Delfino and Enderson,[13] however, have reported that dry ashing techniques provided less complete recovery of the metals from sewage sludge samples. They found that recoveries of chromium, iron and nickel were particularly poor.

The values in Tables V and VI are the relative percent differences of the various results using the nitric acid–hydrogen peroxide digestion as a

TABLE V

Percentage differences of selected metals relative to nitric acid–hydrogen peroxide digestion for primary settling tank sludge

	INAA	Bomb digestion	HNO_3 extraction	Dry ash
Cd		+3.5	−12.7	−17.7
Cr	−78.0	−4.5	+6.4	−18.8
Cu	−6.2	±0.0	−8.2	−24.1
Fe		+2.0	−6.1	−28.4
Ni		−11.7	+19.4	−44.0
Pb		+5.9	−7.8	−16.8
Zn	−2.7	−2.0	−4.0	−6.7

TABLE VI

Percentage differences of selected metals relative to nitric acid–hydrogen peroxide digestion for first-stage digester sludge

	INNA	Bomb digestion	HNO_3 extraction	Dry ash
Cd		+7.5	−6.5	−4.9
Cr	−77.2	−4.1	+7.0	−12.9
Cu	+7.2	+0.7	−3.4	−13.2
Fe		+4.2	−8.5	−37.7
Ni		+1.6	−4.3	−38.0
Pb		+3.7	−7.1	−9.8
Zn	+3.4	−3.1	−1.3	−4.2

reference point. In this reference frame, the results obtained by instrumental neutron activation analysis and by atomic absorption spectrometry after either bomb digestion or nitric acid digestion, agree, for the most part to within 10%, with those obtained after digestion with nitric acid and hydrogen peroxide. The dry ashing procedure, on the other hand, gives rise to results differing, in most instances, by more than 10% from this reference point, and, in all instances, falling below this reference point. While losses by volatilization during the ignition are a possibility, the low results are more likely due to incomplete leaching of the ash with the nitric acid. The ignition at 450° could produce chemical forms not readily soluble in hot, 25% nitric acid.

CONCLUSIONS

Dry ashing is not an acceptable procedure to prepare sewage sludge samples for atomic absorption spectrometry. Digestion of such samples with nitric acid and hydrogen peroxide is an efficient, convenient and rapid procedure for this purpose.

References

1. R. K. Bastian, *Applications of Sewage Sludge to Cropland: Appraisal of Potential Hazards of the Heavy Metals to Plants and Animals* (Report EPA-430/9-76-013, M-33, United States Environmental Protection Agency, Washington, D.C., 1976).
2. R. E. Leffel, *Direct Environmental Factors at Municipal Wastewater Treatment Plants* (Report EPA-430/9-76-003, MCD-30, United States Environmental Protestion Agency, Washington, D.C., 1976).
3. J. Josephson, *Environ. Sci. Technol.* **14,** 38–44 (1980).
4. S. A. Katz and D. M. Scheiner, *Trace Element Levels of Public and Private Potable Water Supplies in Southern New Jersey,* TARC International Symposium III, Halifax, Nova Scotia, August, 1976.
5. T. D. Hinesley, R. E. Thomas and R. G. Stevens, *Environmental Changes for Long-Term Applications of Municipal Effluents* (Report EPA-430/9-78-003, MCD-26, United States Environmental Protection Agency, Washington, D.C., 1978).
6. E. W. Kienholz, G. M. Wood, D. E. Johnson, J. Baxter, G. Braude and G. Stein, *J. Animal. Sci.* **48,** 735–741 (1979).
7. A. Chattopadhyay, *J. Radioanal. Chem.* **37,** 785–799 (1977).
8. C. F. Gurnham, B. A. Rose, H. R. Ritchie, W. T. Fetherston and A. W. Smith, *Control of Heavy Metal Content of Municipal Wastewater Sludge* (Gurnham and Associates, Inc., Chicago, 1979).
9. R. C. Sidel and L. T. Kardos, *Air, Water and Soil Pollution* **8,** 453–459 (1977).
10. T. D. Martin, J. F. Kopp and D. D. Ediger, *Atomic Absorption Newsletter* **14,** 109–116 (1975).
11. S. C. Bergman, C. J. Ritter, E. E. Zamierowski and C. R. Cothern, *J. Environ. Quality* **8,** 416–422 (1979).
12. C. J. Ritter, C. S. Bergman, C. R. Cothern and E. E. Zamierowski, *Atomic Absorption Newsletter* **17,** 70–72 (1978).
13. J. J. Delfino and R. E. Enderson, *Water and Sewage Works* **125,** R32-R34 and R47–R48 (1978).
14. S. Plehn, J. T. Rhett and S. Rondberg, *Process Design Manual, Municipal Sludge Landfills* (Report EPA-625/1-78-010, SW-705, United States Environmental Protection Agency, Washington, D.C., 1979) sec. 3.4.4.
15. R. E. Crowe and A. W. Breidenbach, *Methods for the Chemical Analysis of Water and Wastes* (Report EPA-625/6-74-003, United States Environmental Protection Agency, Cincinnati, 1974).
16. D. R. Ballinger, *Methods for Chemical Analysis of Water and Wastes* (Report EPA-600/4-79-020, United States Environmental Protection Agency, Cincinnati, 1979).
17. L. Kotz, G. Henze, G. Kaiser, S. Pahlke, M. Veber and G. Tolg, *Talanta* **26,** 681–691 (1979).
18. Anon. *Parr Acid Digestion Bombs* (Parr Instrument Co., Moline, IL, 1976) Bulletin 4745.

19. D. G. Ballinger, *Interim Methods for the Analysis of Elemental Priority Pollutants in Sludge* (United States Environmental Protection Agency, Cincinnati, 1978).
20. B. D. Behne and P. Bratter,*Probleme bei der Spuren-elementanalyse in der Medizin, Spurenelemente—Analytick,* Umsatz, Bedarf, Mangel und Toxikologie Symposium in Bad Kissinger, 1977.
21. H. Agemian and A. S. Y. Chau, *Anal. Chim. Acta* **80,** 61–66 (1975).
22. B. Bernas, *American Laboratory* **5,** 41–43 (1973).
23. B. Bernas, *American Laboratory* **8,** 27–32 (1976).
24. A. J. Turnbull, *Chem. Brit.* **15,** 377 (1979).
25. K. W. Budna and G. Knapp, *Z. Anal. Chem.* **294,** 122–124 (1979).
26. M. Oehme, *Anal. Chim. Acta* **109,** 195–197 (1979).
27. M. M. Schachter and K. W. Boyer, *Anal. Chem.* **52,** 360–364 (1980).
28. R. W. Wisseman and S. F. Cook, *Bull. Environ. Contamin. Toxicol.* **18,** 77–82 (1977).
29. M. Zief and J. W. Mitchell, *Contamination Control in Trace Element Analysis* (John Wiley and Sons, New York, 1976), p. 164.
30. M. Hoenig, P. van Hoeyweghen and J. Liboton, *Analusis* **7,** 104–106 (1979).
31. J. L. Fisk, *United States Environmental Protection Agency, Effluent Guidelines,* private communication, 1979.
32. H. R. Watling and I. M. Wardale, Comparison of wet and dry ashing for the analysis of biological materials by atomic absorption spectrometry, L. R. P. Butler, ed., *Analysis of Biological Materials* (Pergamon Press, Oxford, 1979), pp. 69–80.