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A MICROWAVE SYSTEM FOR THE ACID DISSOLUTION OF METAL AND MINERAL SAMPLES

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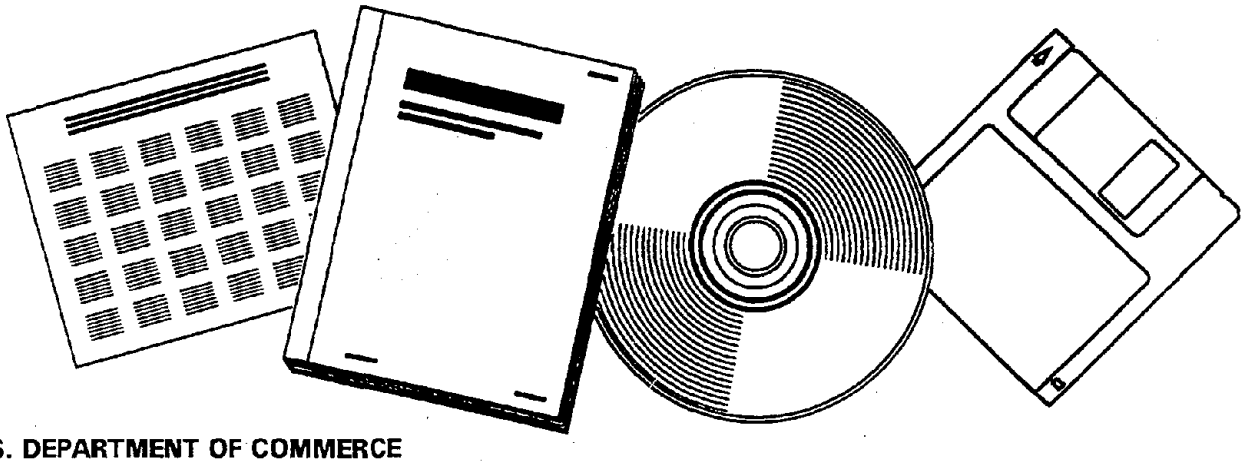

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A MICROWAVE SYSTEM FOR THE ACID DISSOLUTION OF METAL AND MINERAL SAMPLES

by

S. A. Matthes, R. F. Farrell, and A. J. Mackie

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This Bureau of Mines report describes a system for the dissolution of metal and mineral samples using a microwave heat source. Samples and an acid mixture are placed in sealed polycarbonate vessels. The vessel contents are heated using microwaves, digested for 2 min, and quickly cooled. After the solution is brought to a final volume, the vessel contents are heated an additional 2 min in the microwave oven. Using this method, a slag, a feldspar, and a Ni-Cu alloy were dissolved and analyzed by atomic absorption spectroscopy. Values obtained for Na, K, Cu, Ni, Si, Mg, Mn, Ca, Al, and Fe agreed with certified values and had an average relative standard deviation of 1 pct. This system results in a significant savings in time and expense over traditional methods of sample dissolution, and is ideal for preparing solutions for analysis by atomic absorption, plasma optical emission, or X-ray spectroscopy.

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

° C	degree Celsius	mL	milliliter
ft^3	cubic foot	mm	millimeter
g	gram	nm	nanometer
g/L	gram per liter	pct	percent
hr	hour	psi	pound per square inch
mg/L	milligram per liter	W	watt
min	minute	wt pct	weight-percent

A MICROWAVE SYSTEM FOR THE ACID DISSOLUTION OF METAL AND MINERAL SAMPLES

By S. A. Matthes,[1] R. F. Farrell,[1] and A. J. Mackie[2]

ABSTRACT

This Bureau of Mines report describes a system for the dissolution of metal and mineral samples using a microwave heat source. Samples and an acid mixture are placed in sealed polycarbonate vessels. The vessel contents are heated using microwaves, digested for 2 min, and quickly cooled. After the solution is brought to a final volume, the vessel contents are heated an additional 2 min in the microwave oven. Using this method, a slag, a feldspar, and a Ni-Cu alloy were dissolved and analyzed by atomic absorption spectroscopy. Values obtained for Na, K, Cu, Ni, Si, Mg, Mn, Ca, Al, and Fe agreed with certified values and had an average relative standard deviation of 1 pct. This system results in a significant savings in time and expense over traditional methods of sample dissolution, and is ideal for preparing solutions for analysis by atomic absorption, plasma optical emission, or X-ray spectroscopy.

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INTRODUCTION

One goal of the Bureau of Mines is to investigate technology to insure a dependable supply of minerals to the United States. To support this goal, the Bureau is conducting research related to the improvement of analytical procedures used to characterize metal and mineral samples. In particular, this research is directed to the reduction in time, complexity, and expense of sample dissolution for chemical and instrumental analysis.

The rapid development of automated instrumentation has enabled the analytical chemist to perform an ever-increasing number of analyses. Unfortunately, sample preparation has not kept pace with the development of analytical instrumentation.

The Bureau previous investigated a method for the rapid, low-cost dissolution of samples in plastic pressure vessels.[3] The method consisted of acid digestion in sealed plastic bottles that were heated in a boiling water bath. After digestion the samples were water cooled. Boric acid solution was then added to each bottle, and the solutions were reheated in the boiling water bath to dissolve any precipitated fluorides. Because dissolution was carried out in closed plastic vessels, contamination was avoided and volatile gases such as SiF_4 were retained. Samples could be prepared for analysis in less than an hour, and many elements could be analyzed from this single dissolution. In an effort to speed up dissolution time even further, the Bureau has introduced a significant improvement by using a microwave oven as a heating source.

One problem characteristic of microwave ovens is the presence of "hotspots" in the oven, which cause uneven heating. To overcome this problem Bureau personnel designed a polypropylene rack to fit atop a standard microwave carousel. With the bottles evenly spaced on the rack, each is subjected to the same amount of heating energy as the carousel turns automatically. Polypropylene was chosen for the rack because (1) it is inexpensive and easily worked, (2) it is acid-resistant and transparent to microwaves, and (3) it is strong enough to be used for transporting the bottles. No such rack was commercially available.

Another modification of the system is the use of a stream of CO_2 gas, rather than the water bath, to cool the bottles and help remove any possible acid fumes from the microwave oven after the dissolution step. This technique is faster, safer, and more convenient with regard to the microwave oven than water. Because CO_2 is stored in liquid form, it flows from the cylinder at a temperature lower than that of compressed air, a third alternative for cooling the bottles.

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[3]Farrell, R. F., S. A. Matthes, and A. J. Mackie. A Simple, Low-Cost Method for the Dissolution of Metal and Mineral Samples in Plastic Pressure Vessels. BuMines RI 8480, 1980, 14 pp.

Matthes, S. A. Rapid Low-Cost Analysis of a Copper Slag for 13 Elements by Flame Atomic Absorption Spectroscopy. BuMines RI 8484, 1980, 8 pp.

EXPERIMENTATION

EQUIPMENT

1. Shatter box grinder.

2. Polycarbonate bottles, 250 mL, with polypropylene screw caps. (Nalge[4] #3122-0250 or IEC #2051; see appendix.)

3. Polypropylene bottle holding rack constructed from 1/16-inch polypropylene sheet (figs. 1 and 2). (A complete description of the fabrication of this rack is available on request from the authors.)

4. A 1- to 100-mL precision liquid dispenser.

5. A 1.4-ft^3-capacity microwave oven (650-W maximum power) with removable carousel.

6. Atomic absorption spectrophotometer with microprocessor, curve correction, and digital readout.

7. A 50-mm nitrous oxide burner head.

8. Hollow cathode lamps for Mg, Ca, Al, Si, Fe, Na, K, Cu, Ni, and Mn.

9. Welder-grade C_2H_2, high-purity N_2O, dry and oil-free compressed air, and CO_2.

[4]Reference to specific equipment, trade names, or manufacturers is made for identification only and does not imply endorsement by the Bureau of Mines.

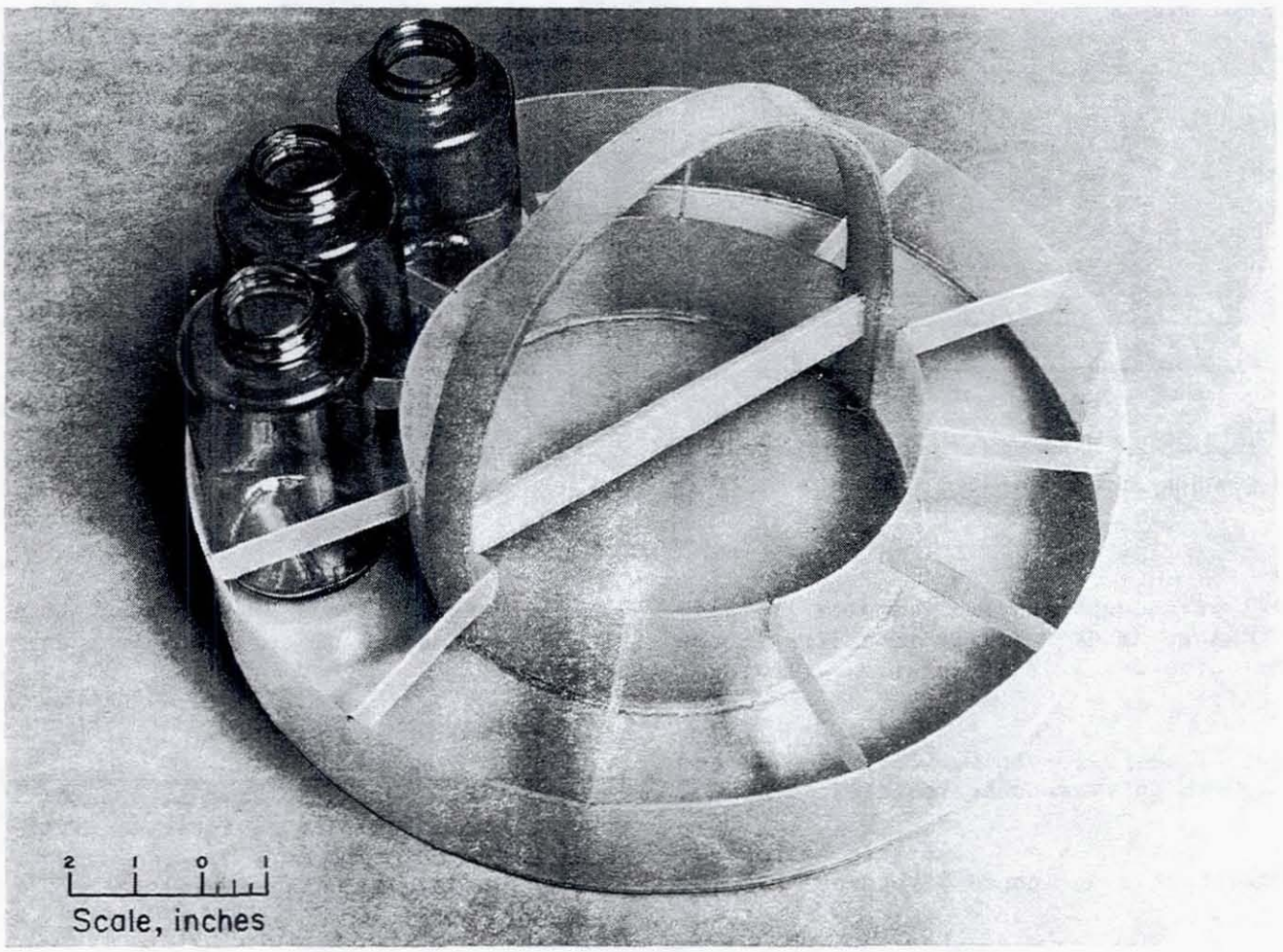
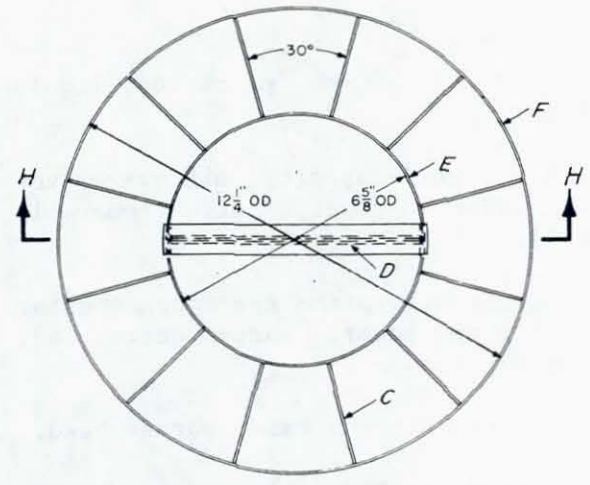
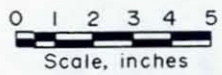


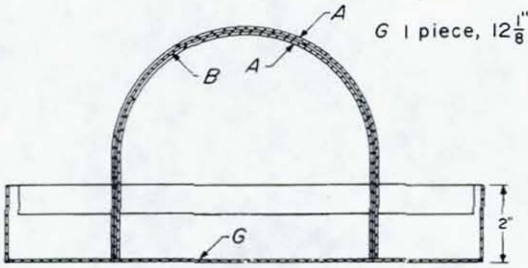
FIGURE 1. - Polypropylene microwave-transparent bottle holding rack.



Fabricate bottle rack from $\frac{1}{16}$-inch sheet polypropylene



A 2 pieces, $\frac{3}{4}$" x 17"
B 1 piece, $\frac{3}{4}$" x 13"
C 12 pieces, $\frac{1}{2}$" x 2$\frac{3}{4}$"
D 3 pieces, $\frac{3}{4}$" x 6$\frac{3}{4}$"
E 1 piece, 2" x 21$\frac{1}{2}$"
F 1 piece, 2" x 38$\frac{3}{4}$"
G 1 piece, 12$\frac{1}{8}$" OD



Section H-H

FIGURE 2. - Dimensions of polypropylene bottle holding rack.

REAGENTS AND SOLUTIONS

1. Boric acid solution (1.5 wt pct) made by mixing 60 g of high purity boric acid crystals (99.99 pct) with 4,000 mL of H_2O.

2. (a) HCl-HF mixture (7:3) made up with concentrated, reagent-grade acids.

   (b) HNO_3--concentrated, reagent-grade acid.

3. Primary standard solutions of 1,000 mg/L were prepared for each element from high-purity (99.9 pct) materials.[5]

MICROWAVE DISSOLUTION APPARATUS

The dissolution system consists of microwave oven vented to a fume hood, the bottle-holding rack, the carousel, and the CO_2 cylinder (fig. 3). All exposed metal parts inside the microwave oven were covered with plastic tape to prevent corrosion. A small hole was drilled in the back of the oven, through which tubing was run from the regulator on the CO_2 cylinder. The tubing was anchored and positioned so that when the CO_2 was flowing, the gas would strike and cool each bottle as the rack turned on the carousel. (See figure 4.) The exhaust vent on the oven was connected to the exhaust stack of a fume hood by a flexible plastic hose so that the CO_2 and any acid fumes would be quickly evacuated from the oven. After all modifications were made to the microwave oven, the system was tested for radiation leaks. None were detected.

METHOD

1. Grind nonmetallic samples to pass 100 mesh. Metal samples should be in the form of powder, fine shavings, turnings, or wire.

2. Place 0.100- to 0.500-g samples into 250-mL polycarbonate bottles.

3. Pipet (using a plastic pipet or other precision liquid dispenser) a 5-mL, 7:3 mixture of HCl and HF into each bottle, then add 2 mL of HNO_3 into each bottle.

4. Screw caps on tightly.

[5]Smith, B. W., and M. L. Parsons. Preparation of Standard Solutions, Critically Selected Compounds. J. Chem. Ed., v. 50, No. 10, 1973, pp. 679-681.

FIGURE 3. - Microwave dissolution system including microwave oven, bottle rack and carousel, and CO_2 cylinder. Also pictured (center right) is the precision liquid dispenser for the addition of boric acid solution.

5. Put bottles into bottle-holding rack and place rack on the carousel in the microwave oven. Heat on high power for 2 min. Heating time may vary, but 1 to 3 min is sufficient for most samples.

6. After completion of heating cycle, cool the bottles for approximately 1 to 2 min. (Line pressure of CO_2 should be approximately 40 psi.).

7. Remove rack and bottles from the microwave oven and add 93 mL of a 1.5-pct-H_3BO_3 solution to each bottle, using a precision liquid dispenser.

8. Screw caps on tightly.

9. Put the rack and bottles back on the carousel in the microwave oven and heat for 2 min.

10. Remove rack and bottles checking for undissolved residue. If necessary, return to microwave oven and heat an additional 1 to 8 min to achieve dissolution.

11. When the solutions are cool, they are ready for analysis. Bottles may be cooled quickly in a coal water bath, if desired.

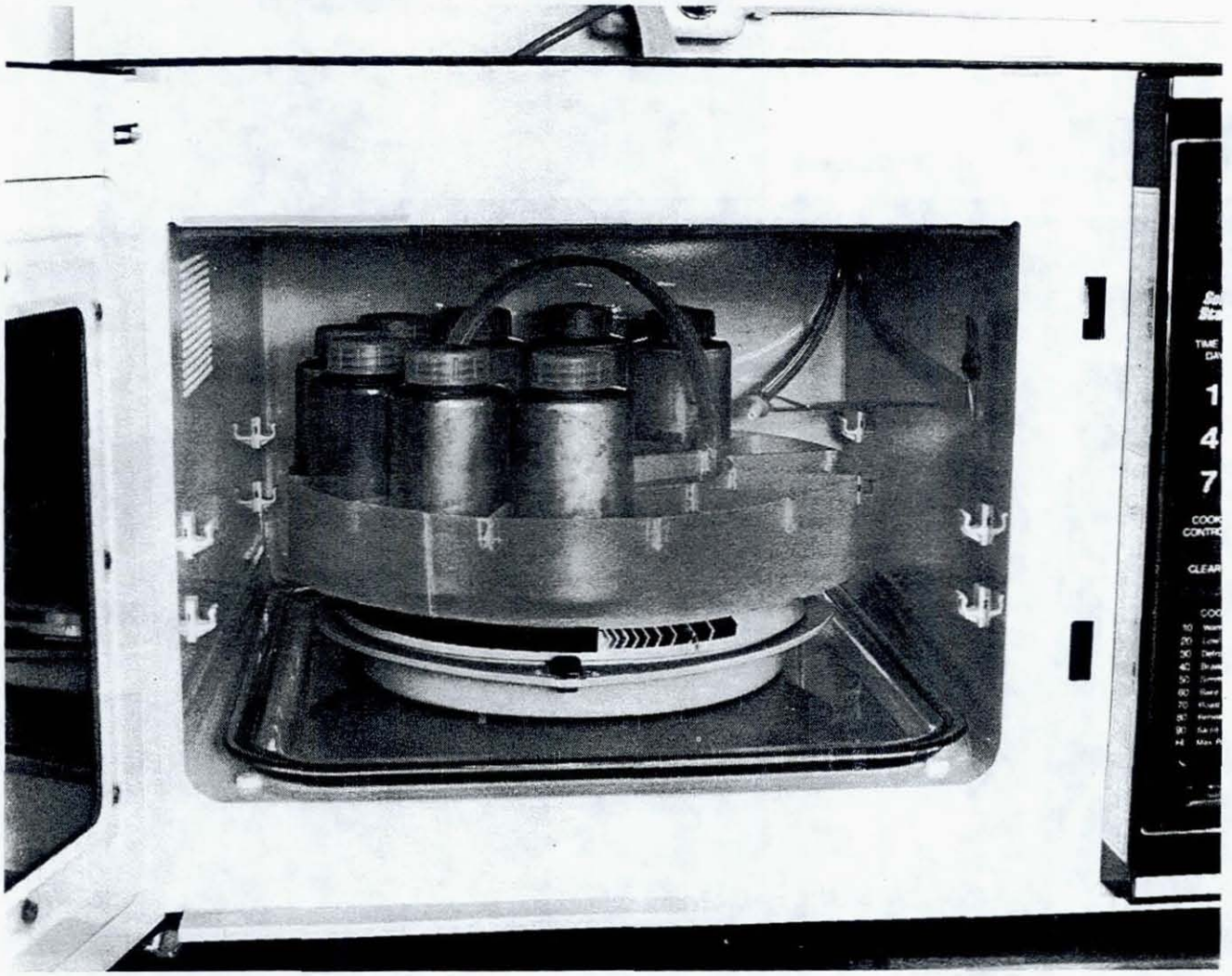


FIGURE 4. - Closeup of microwave oven showing positioning of CO_2 gas flow (upper right corner of cavity) for cooling bottles.

RESULTS

The microwave dissolution method was used to prepare solutions from the Brammer Standard Co. basic oxygen furnace slag and two National Bureau of Standards reference materials. After the appropriate dilutions, these solutions were analyzed by flame atomic absorption spectroscopy. Standards were not corrected for matrix effects. Four samples from each material were analyzed from separate bottles, and the average wt pct and relative standard deviation (RSD) were calculated. The results are given in tables 1, 2, and 3. A sample weight of 0.20 g was used for the slag and the Ni-Cu alloy, while 0.10 g was used for the feldspar.

The tables show that the samples are in excellent agreement with the certified values. Relative standard deviations ranged from 0.0 to 3.92 pct, with an average of 1.09 pct. These values were obtained using standards uncorrected for matrix effects. Mg, Ca, Al, Si, and Fe were determined using a N_2O-C_2H_2 flame, and Mn, Na, K, Cu, and Ni were determined using an air-C_2H_2 flame. Ionization effects in the analysis of Ca and Al were corrected by the addition of 0.8 g/L and 4 g/L NaCl to sample and standards for Ca and Al, respectively.[6] Mg, Ca, Al, Na, K, and Cu were run using 0.7-nm slit, and Fe, Mn, Si, and Ni were run using a 0.2-nm slit.

[6]Works cited in footnote 3.

TABLE 1. - Analytical data from analysis of basic oxygen furnace slag, Brammer standard #101/1, wt pct

	FeO	MgO	CaO	SiO_2	MnO
Average.....	7.94	9.19	50.2	23.8	3.84
RSD.....	1.64	.78	.48	1.21	.00
Certified value...	8.04	9.15	52.4	23.7	3.45

TABLE 2. - Analytical data from analysis of NBS #70A (potassium feldspar), wt pct

	Na_2O	K_2O	SiO_2	CaO	Al_2O_3
Average.....	2.66	12.0	65.6	0.13	17.5
RSD.....	.53	.42	1.17	3.92	1.68
Certified value...	2.55	11.8	67.1	.11	17.9

TABLE 3. - Analytical data from analysis of NBS #162A (nickel-copper alloy), wt pct

	Cu	Ni	Mn	Fe	Si	Al
Average.....	29.6	62.9	1.68	2.20	0.97	0.51
RSD.....	.43	1.46	.35	.00	1.95	1.60
Certified value...	30.6	64.0	1.60	2.19	.93	.50

DISCUSSION

Pressure dissolution in plastic vessels has been used by the Bureau for over 6 years. The method presented here has been used successfully for the past year on a wide variety of samples including glasses, clays, slags, mattes, metals, and silicate materials. The microwave oven provides extremely rapid heating and better control of both heating time and power than previous methods.[7] Because the microwave radiation generated from a microwave oven spans a narrow range of frequencies, the radiation couples with and excites only a few types of molecules. Specifically, microwave ovens are designed to excite water and other molecules containing similar chemical bonds. There are large numbers of substances, chiefly glasses, ceramics, and plastics, that will not couple with the microwave radiation and are essentially microwave transparent; that is, the microwaves pass through without heating them.

The polycarbonate vessels used in the previous method are transparent to microwaves, allowing the adoption of the microwaves as a heating source for the dissolution. Microwave radiation passes through the polycarbonate and couples with and excites the water and acid molecules of the $HCl:HF:HNO_3$ mixture. Because this heating process is by a direct coupling and not by convection or conduction, sample dissolution is greatly speeded up. Heating time and power are very precisely controlled on the microwave oven by a built-in microprocessor. Heating temperatures are therefore not limited by the temperature of a heating bath, but by the maximum power output of the microwave oven, the boiling point of the solution, and the ability of the container to hold pressures. By eliminating the hot and cold water baths, the method requires much less space and is neater and more convenient to use. Gas cooling allows the immediate addition of boric acid after the dissolution step. Because the acid is in contact with plastic bottles for shorter periods, bottle life is extended.

The microwave dissolution procedure described in this report has been tested rigorously for safety. The bottle rack will contain any acid spills due to bottle failure; acid fumes are routed

[7]Works cited in footnote 3.

through the oven exhaust vent into a fume hood; and the door of the microwave oven prevents acid fumes from escaping during dissolution. The recommended bottles, which were designed for use in a centrifuge, are very strong and have proven satisfactory during an extended trial period. In the time during which this procedure has been in use, bottle failures, which consist typically of cracking at the bottle base, have been infrequent. Pressures generated during the dissolution step are insufficient to cause explosions; however, because of the extremely rapid heating of microwave ovens, care must be taken not to exceed the recommended heating time. Excessive heating can lead to bottle failure. (See appendix.).

CONCLUSIONS

A system has been presented for dissolution of metal and mineral samples using microwave heating. The method is suitable as a general dissolution procedure for a wide range of sample types. This system has many advantages over traditional methods of sample preparation, including:

1. Microwave ovens are a fast, convenient, and inexpensive way to heat liquids, allowing precise control of heating power and time.

2. Polycarbonate is transparent to microwave radiation; the acid is heated without first having to heat the bottle.

3. The bottle holding rack is transparent to microwaves and is strong enough to serve additionally as a bottle transport rack to and from balances and instruments. Its design allows even heating (with the use of a carousel) of the bottles during the heating cycle. Any acid leaks caused by bottle failure are contained, protecting the microwave oven. Acid fumes are quickly removed into the laboratory exhaust systems.

4. The use of gas cooling eliminates the inconvenience and mess of water cooling in between the acid additions.

5. The use of closed plastic dissolution vessels prevents the introduction of contaminating elements and the loss of volatile elements and compounds.

6. A batch of samples can be dissolved for analysis in approximately 5 min in a safe and inexpensive manner. Open dish preparation using a conventional hotplate may take several hours, and pressure dissolution using a hot water bath may take approximately 1 hr.

7. When recommended procedures and bottles are used, this method is an inexpensive, fast, and safe way to dissolve a wide variety of sample types for analysis.

APPENDIX.--POLYCARBONATE BOTTLES

Polycarbonate is an inexpensive, high-tensile-strength, heat- and acid-resistant plastic; it is transparent, rigid, unbreakable, nontoxic, and microwave transparent. Using the recommended equipment and acid mixture, bottle lifetime should be about 10 runs. A gradual yellowing and increasing opaqueness of the plastic is normal with bottle use. Bottles occasionally will fail by cracking at the bottom. Internal pressure inside the bottles during dissolution is not sufficient to cause an explosion. The microwave-transparent rack will contain any spills due to bottle failure.

The melting point of polycarbonate is 135° C; but is is recommended that a maximum working temperature of 120° C be used. Care must be taken to insure that the contents of the polycarbonate bottles remain below this temperature while using the high power settings on the microwave oven.

Both acid volume and sample weight may be safely varied in the method; however, it is recommended that a maximum of 10 mL of acid be used to dissolve samples of up to 1 g. Using the 7-mL acid mixture of the method presented, a maximum sample weight of 0.500 g is recommended. Some samples, particularly those high in silicon, will require smaller sample weights for dissolution.

During the dissolution process, some acid fumes will leak around the caps of the bottles. Although this leakage does not affect the analytical results, it creates a health hazard, requiring the microwave oven to be vented to a fume hood.

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