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APPLICABILITY OF THE RF-FURNACE TECHNIQUE FOR AA AND AE ANALYSES OF TRACE ELEMENTS IN ENVIRONMENTAL SAMPLES

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ABSTRACT

The application of the RF-Furnace, for direct analysis of solids or evaporated solutions by atomic emission and atomic absorption spectrometry, is described. Various sample pretreatment procedures for environmental as well as inorganic samples are compared. Direct analysis of solids is possible but precision and accuracy are limited by the inhomogeneity of the solid microsample. Accuracy on the order of 8% has been obtained with "real" environmental samples. Absolute sensitivities on the order of 10^{-10} to 10^{-12} gm have been obtained for Cd, Zn, Pb, and Cu. Since samples can be introduced at a rate of several per minute, the method shows great potential for routine analysis.

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[1] Operated by Union Carbide Corporation for the USAEC.

INTRODUCTION

Today both atomic emission (AE) and atomic absorption (AA) spectrophotometry are widely accepted methods for elemental analysis. Even with the massive influx of plasma and nonflame techniques now available, the flame is still the most widely accepted. This is true because the characteristics of the flame are well defined and controlled, the flame techniques are both technically and methodically simple, analytical reproducibility is satisfactory, and a wide variety of commercial instrumentation is available.

The various nonflame atomic absorption devices and plasma emission sources are attempts at improvement and replacement of the well established flame techniques. The nonflame atomizers of L'vov (1), Massmann (2), Woodriff (3), West and Williams (4), and others have been shown to have exceptional sensitivity for the atomic absorption determination of trace elements while the plasma excitation sources of Runnells and Gibson (5) and Fassell and Dickinson (6) have been shown to have a similar improvement in sensitivity in the atomic emission mode.

The Radio-Frequency Furnace Source (RFF) (7), is unique in that it can operate alternately in either atomic emission or atomic absorption modes. Optimization for either mode is simply a matter of selecting the proper induction coil and crucible design.

MATERIALS AND METHODS

Figure 1 shows the overall system schematic. The location of system components is similar to that of a conventional flame spectrometer except that the RFF source replaces the burner. In the atomic absorption mode, light from a hollow cathode lamp is focused at the center of the RFF with one lens and then refocused at the entrance slit of the monochromator with a second lens.

Fig. 1

Figure 2 is a photograph showing the actual location of the various components. The RF generator (Lepel Model T-7.5-3-MC-A-SW) is connected to a 1/4" I.D. copper induction coil which usually consists of four turns for AA and five or more turns with one turn above the sidearms for AE. Hollow Cathode lamps serve as the primary source for AA. The detection system, not shown, is to the right, adjacent to the monochromator (0.5 Meter Ebert Mount, Jarrell Ash Model 82-000).

Fig. 2

Figure 3 is a drawing of the heart of the system. A graphite crucible, coated inside and out with high density pyrolytic carbon and surrounded by a layer of insulating carbon black, is centered in a Vycor thimble. This thimble is inserted inside a Vycor reaction tube which has side arms with quartz windows at each end. The graphite crucible can be raised to and maintained at temperatures of up to 2500°C by the induction furnace. When in operation, the reaction tube is continuously flushed with helium or a mixture of helium and argon. The crucible design used in the atomic absorption mode has a pair of windows drilled in the upper part so that light from the primary source can pass through. Crucibles used in atomic emission have no windows and are packed so that the optical path grazes the crucible top.

Fig. 3

The hot graphite crucible serves as the principal source of atomization. Excitation for AE is possible when, with the proper choice of induction coil, a helium discharge plasma is formed at the mouth of the crucible.

Sample introduction is accomplished in the following manner. A liquid sample is transferred or a solid sample is weighed onto a tantalum planchet-cup. The sample is dried on the planchet at a suitable temperature by means of a hot plate. This dried sample is placed into the sample introduction chamber, inserted to a position directly above the crucible mouth, and dropped. As the atomized sample is flushed from the crucible into the optical path by the inert gas stream, either AA or AE measurements can be made. In either case, the signal is detected by a photomultiplier (1P28), amplified by a picoammeter (Keithley Model 409), and displayed on an oscillographic chart recorder (Sanborn Model 150).

Reagents: The H_2O, HNO_3, and $HClO_4$ used in standard preparation and wet ashing procedures were either triple distilled or analyzed for purity prior to use. "Soluene 100", a quaternary ammonium hydroxide prepared as a xylene and toluene solution by Packard Scientific, or a 25% solution of tetramethyl ammonium hydroxide in ethanol, served as a tissue solubilizer (8). Copper, lead, cadmium, and zinc stock solutions were made from 1% atomic absorption standards produced by Fisher Scientific.

Sampling Devices: Solutions of 0.5-25 µl volume were transferred to the planchets by means of a microsyringe. These microsyringes were fitted with teflon plunger tips or teflon tube-needles in order to prevent or minimize syringe deterioration and sample contamination, especially when dealing with highly acidic solutions. Solid samples, in the form of fine powders, were weighed directly onto the planchets and immobilized with 1-2 µl of dilute collodion solution.

Tantalum Planchets: Tantalum planchets of 1/8 - 5/16" diameter were punched from 0.005" thick tantalum. To reduce trace contamination from these planchets, up to 1,000 at a time were placed in a pyrolytic carbon coated crucible and were prebaked in the RFF at 1500-1800°C for 20 minutes prior to use. Several hundred planchets can accumulate in the crucible during analysis before removal is required.

Sample Pretreatment:

1. Direct Analysis. Liquids such as oil and gasoline, (1-20 volumes), and solids such as freeze dried liver, coal and soil (0.1-3 mg) were transferred to the planchets as described above. All organic samples were ashed, on the planchets, in a muffle furnace at 450-500°C for 8-12 hours before analysis.

2. Wet Ashing: Freeze dried biological materials (liver, leaves, potatoes), oil and gasoline were digested with concentrated HNO_3 and $HClO_4$. No more than 2 gm of material were dissolved in 15 ml of HNO_3; 15 ml of $HClO_4$ was added when the HNO_3 digestion was complete (9,10). The solution thus produced was diluted to a suitable final volume of 25, 50, or 100 ml. Blank solutions and solutions for recovery studies were treated in an identical manner. Then, 1-20 µl aliquots were transferred to the planchets arranged on a pyrex plate. The samples were slowly dried at temperatures up to 225°C.

3. Tissue Solubilization in "Soluene 100". The application of Soluene to the solubilization of fresh animal tissue was reported previously (11). This study extends the applicability of soluene to freeze dried material. A 0.5 gm sample of NBS Material 1577 (liver), was dissolved in 10 ml of Soluene at 70°C during an 8 hour period. Aliquots of 1-20 µl of this solution were transferred to the planchets, dried and ashed as described above.

RESULTS AND DISCUSSION

Instrumental Parameters: For AE measurements, a 5-7 turn induction coil with one turn above the reaction tube sidearms produced a sufficiently intense discharge plasma to excite the elements in this study. On the other hand, a four turn coil has been found to heat the crucible very efficiently without simultaneously producing a discharge, an optimum condition for AA.

It has been previously reported (7) that shorter crucibles produce more sensitive and precise results. Consequently, all current work has been done with crucibles 1-3/4" long by 5/8" in diameter. In absorption studies using the crucible with a hole or "window", it is believed that a higher mean temperature is maintained in the optical path, because one observes improved sensitivities and reduced molecular absorption-scattering interferences with this configuration. For example, the measured absorbance for 50 μg of NaCl at the 213.8 nm Zn line was reduced from 0.08 to 0.03 and sensitivities for Cd and Zn were increased from 20 to 5 pg.

Detection Limits: The atomic absorption sensitivity, defined as the amount of the element which results in 1% absorption is 5 pg for both Cd and Zn and 50 pg for both Pb and Cu. The atomic emission detection limit, defined as the amount of element which produces a signal twice the size of that obtained from distilled water blanks, is 6 and 8 pg for Cd and Zn respectively and 80 pg for Pb.

Analytical Working Curves: Analytical curves obtained for Cd and Zn by AA at their respective 228.8 and 213.7 nm lines were linear at the tested 10-1000 pg range and passed through the origin. The curve for Pb at 217.0 nm was linear from 100 to 5000 pg with curvature toward the concentration axis above this range. The working curve for Cu at 324.7 nm was linear from 100 to 10,000 pg. Both curves passed through the origin.

Working curves for Cd and Zn obtained by AE at their 326.1 and 305.7 nm lines respectively, were linear from 20 pg to 1 μg and similarly passed through the origin.

Analytical Procedures: The analytical procedure for most non-flame techniques involves the introduction of a liquid sample into an atomization chamber, followed by a drying-ashing-atomizing cycle. Consequently, the accuracy and precision of the results are highly dependent upon sample volumes used and their physical location within the atomizing device (12). The RFF, on the other hand, allows separation of the cycle into its discrete analytical steps. A large number of samples may be transferred first to the tantalum planchets, dried and ashed and then analyzed at the rate of several per minute. Thus, the actual time spent operating the instrument is greatly reduced. Further, it has been noted that this separated three step cycle may reduce matrix interferences (13).

Accuracy and Precision: Tables I through IV summarize the results of determinations of Cd, Zn, Pb, and Cu in a variety of materials including animal and vegetable tissue, fossil fuels both refined and unrefined, and inorganic samples such as soil and fly ash. Accuracy of Cd determinations vary from 0% (coal) to 35% (fly ash) with an overall accuracy of 8.2% if gasoline is omitted. These estimates of accuracy are all based upon the assumption that the independent value is the correct one. The systematically lower results obtained for gasoline indicate possible losses of volatile Cd compounds in the drying step or in the transfer of the volatile sample to the planchets, or both.

The accuracy of the Zn determinations range from 0% to 20%, averaging 6.8%. The overall average relative standard deviation for the four tables was less than 3% and ranged from 1.6% to 10.7%.

(Place Tables
I thru IV here)

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Interferences: Non-specific spectral interferences, such as molecular absorption and scattering were characteristic of the AA mode while non-specific vapor phase interferences, i.e., changes in the excitation parameters of the RF plasma, were observed in the AE mode. A more detailed analysis of these interferences was presented in previous papers (7).

Typical of the results of interference studies were those for Pb. The presence of a 4000 fold excess of such common interferences as Ca, Mg, Al, and Fe changed measured absorbances a maximum of ±.03 absorbance units with ±.01 being typical.

The substantial reduction of AA interferences compared to other nonflame techniques greatly compensates its poorer absolute sensitivity.

The interferences in the atomic emission mode are more severe and therefore the standard addition technique is generally recommended for samples containing complex matrices.

Comparison of Sample Pretreatments: Each pretreatment procedure has advantages as well as certain disadvantages. A careful examination of each gives the following apparent conclusions.

1. The wet ashing method provides maximum accuracy and precision. However, unless followed by extraction, the sensitivity available is limited. This limitation is more critical as one approaches the detection limit.

2. The soluene procedure serves as a good substitute for wet ashing. It is the procedure least susceptible to contamination from dust fall, because the solubilizing may be carried out in a sealed flask. It would seem especially applicable to resistance furnace techniques.

3. Direct analysis, although very appealing, may become impractical due to random errors introduced by the weighing procedure and inhomogeneity of small solid samples. Of these, the latter error is most serious. The homogeneity of a powdered sample is closely related to its size, its average particle size, the chemical state of the analyte, and the analyte concentration.

The coefficient of variation for a series of measurements of an analyte in a given matrix is inversely proportional to the size of the sample and also inversely proportional to the square root of the number of particles in that sample. Since the practical sample size is limited to 0.1-10 mg, homogeneity can only be improved by grinding the sample, i.e., increasing the number of particles. Table V shows the effect of this parameter. The coefficients of variation were calculated to be 26.5%, 15.6%, 7.2%, and 6.5% for the coal, crushed coal, fly ash and orchard leaves, respectively. It should be noted that there is a point of diminishing returns that can be obtained by grinding. This critical value of particle size is also dependent upon the chemical nature and concentration of the analyte as well as upon the nature of the matrix.

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V here.

CONCLUSION

In summary, although absolute sensitivities are generally inferior when compared with other nonflame systems, matrix interferences are substantially lower and larger size samples can be analyzed. The RFF system shows considerable potential for the rapid and routine analysis of Cd, Zn, Pb, and Cu in a wide variety of environmentally based samples. Relatively few requirements for the pretreatment of the samples significantly shortens the analysis time, while accuracy and precision are generally more than adequate.

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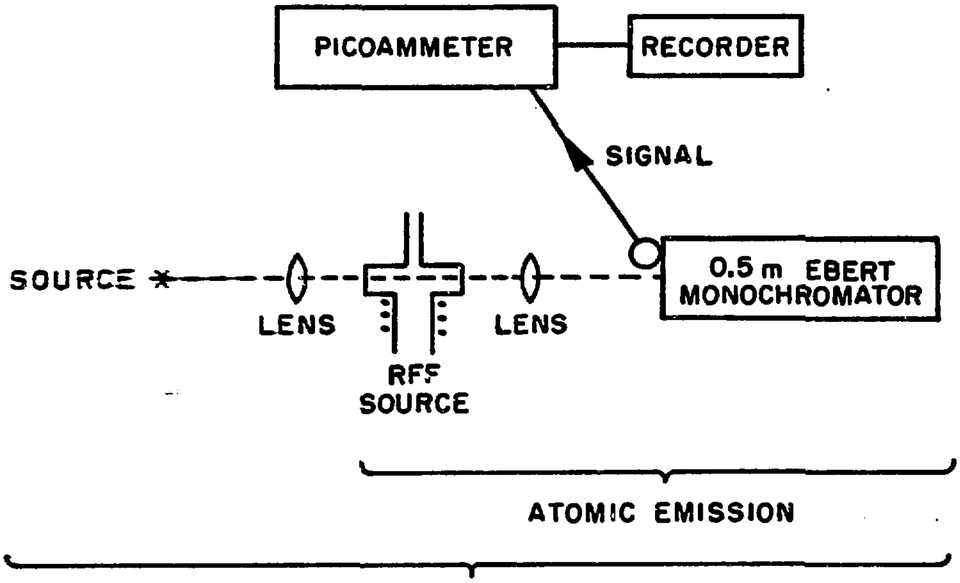

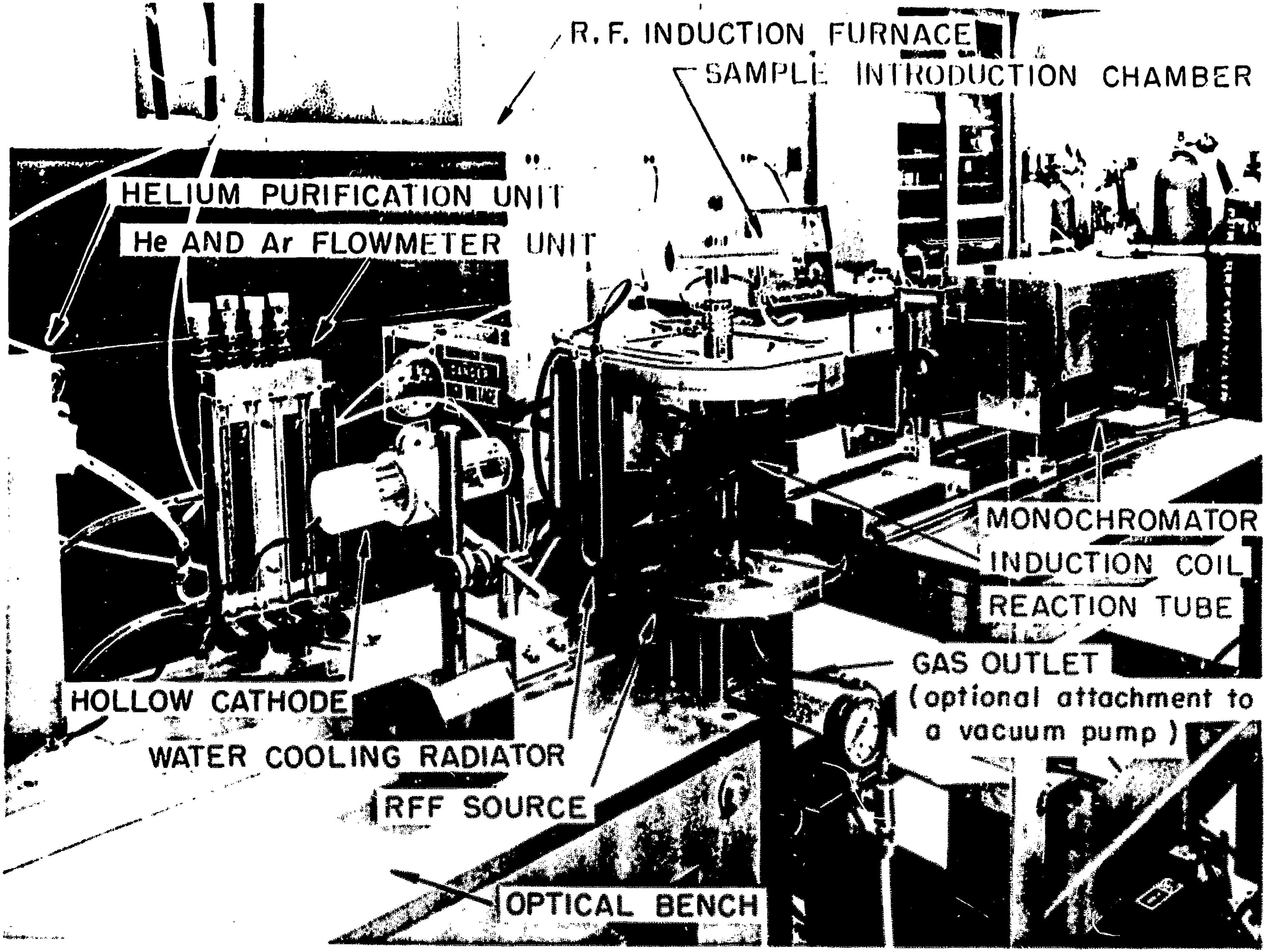
R.F. INDUCTION FURNACE
SAMPLE INTRODUCTION CHAMBER
HELIUM PURIFICATION UNIT
He AND Ar FLOWMETER UNIT
MONOCHROMATOR
INDUCTION COIL
REACTION TUBE
GAS OUTLET
(optional attachment to a vacuum pump)
HOLLOW CATHODE
WATER COOLING RADIATOR
RFF SOURCE
OPTICAL BENCH

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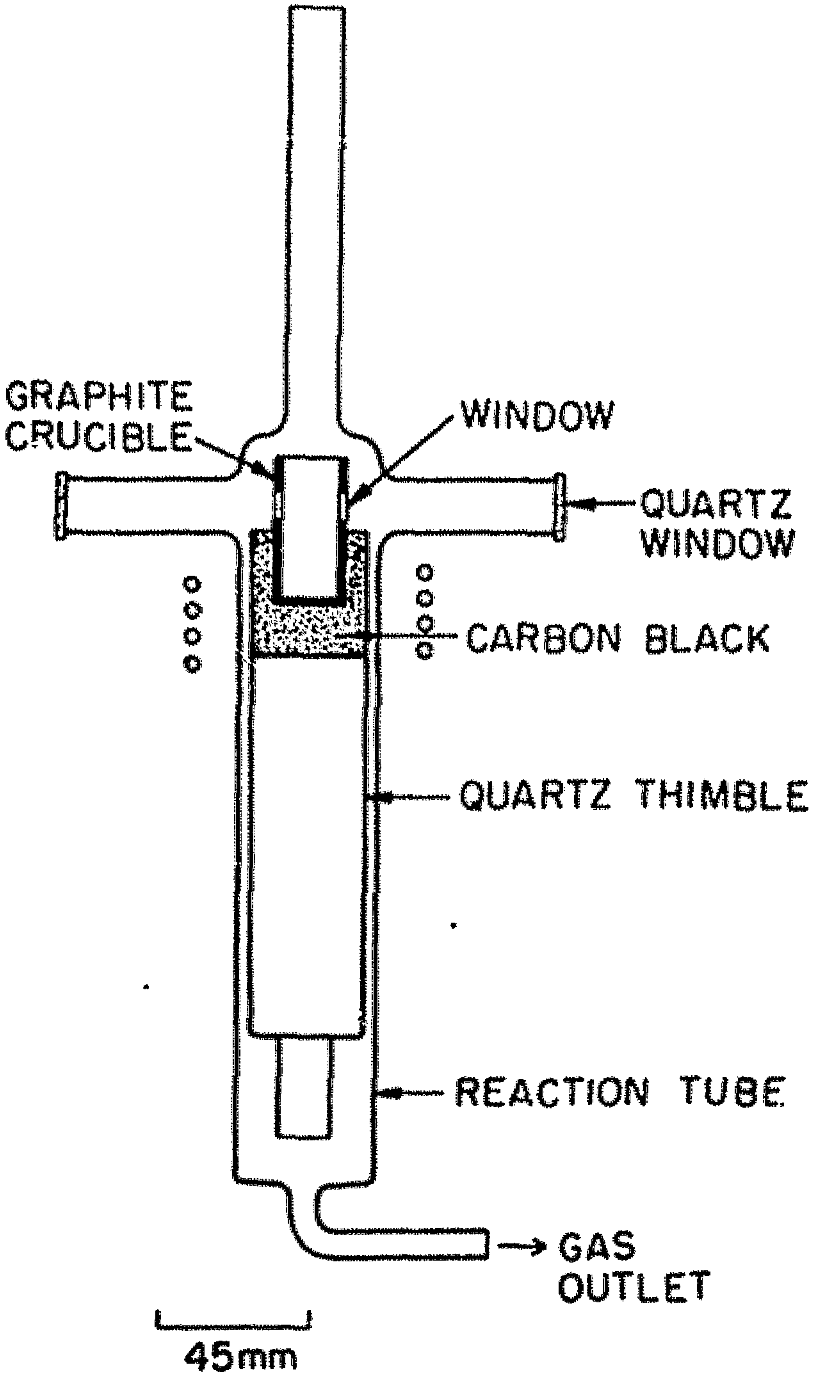

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Table I. Determination of cadmium in environmentally based materials

Sample	Average sample size, gm	Pretreatment procedure	Spectrometric mode	Concentration of Cd found, ppm	Known concentration, ppm	Independent method
Coal, NBS	3	WA	AA	0.30 ± 0.01	0.30	SMS
	0.0002–0.0015	D	AA	0.28 ± 0.03		
Fly ash, NBS	2.4	WA	AA	1.8 ± 0.09	1.5 –2.2	SMS
	0.0002–0.0015	D	AE	1.9 ± 0.15		
	1.5	L	AA	1.2 ± 0.04		
Bunker oil	1.8	WA	AA	0.85 ± 0.03	0.83	SMS
Gasoline #1	0.005–0.01	D	AA	0.0078 ± 0.0007	0.018	SMS
#2	0.005–0.01	D	AA	0.00070 ± 0.0006	0.017	SMS
#3	0.005–0.01	D	AA	0.0085 ± 0.0007	0.020	SMS
Soil #1	0.31	L	AA	0.42 ± 0.02	0.38	
#2	0.25	WA	AA	0.95 ± 0.04	0.78, 1.05	SMS, FAA
#3	0.32	WA	AA	0.41 ± 0.02	0.36, 0.48	SMS, FAA
Bovine liver, NBS	1.5	WA	AA	0.29 ± 0.013	0.27	NBS
	0.5	SS	AA	0.30 ± 0.018		
	0.0002–0.0015	D	AA	0.32 ± 0.025		
Orchard leaves, NBS	1.5	WA	AA	0.13 ± 0.005	0.11	NBS
	0.0002–0.0012	D	AA	0.13 ± 0.007	0.14	SMS
Fish gonad #1	1.3	WA	AA	0.73 ± 0.03	0.7	FAA
#2	2.7	WA	AA	0.84 ± 0.07	0.8	FAA
#3	2.0	WA	AA	1.16 ± 0.04	1.3	FAA

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Table II Determination of zinc in environmentally based materials

Sample	Average sample size, gm	Pretreatment procedures	Spectrometric mode	Concentration of Zn found ppm	Known Zn concentration, ppm	Independent method
Coal, NBS	3	WA	AA	43.4 ± 1	41	FAA
Bunker oil	1.8	WA	AA	1.9 ± 0.06	1.7 ± 0.03	APDC-MIBK
Soil #1	0.25	L	AA	85 ± 3.5	87	SMS
		L	AE	89 ± 6		
Bovine liver, NBS	1.5	WA	AA	126 ± 4	130 ± 10	NBS
	1.5	WA	AE	134 ± 5		
	0.5	SS	AA	124 ± 7		
	0.0002–0.00015	D	AE	134 ± 10		
Orchard leaves, NBS	1.5	WA	AA	27 ± 2	25 ± 3	NBS
	0.0002–0.0012	D	AE	28 ± 3		
Fish gonad #1	1.3	WA	AA	12 ± 0.4	10	FAA
#2	2.7	WA	AA	47 ± 2.0	49	FAA
#3	2.0	WA	AA	28 ± 1.1	28	FAA

Table III. Determination of Pb in environmentally based materials

Sample	Average Sample Size, gm	Pretreatment Procedure	Spectrometric Mode	Concentration of Pb Found, ppm	Known Concentration ppm	Source
Coal, NBS	0.92	WA	AA	29 ± 0.5	30 ± 10	NBS
Soil						
C-19	1.40	WA	AA	41 ± 1	48	SSMS
C-30	1.44	WA	AA	42 ± 1	46	SSMS
Material 1571 (Orchard Leaves)	.40	WA	AA	45 ± 0.5	45 ± 3	NBS
Light Oil (Spiked)	1.52	WA	AA	5.1 ± 0.1	5.5	

Table IV. Determination of Cu in environmentally based materials

Sample	Average Sample Size, gm	Pretreatment Procedure	Spectrometric Mode	Concentration of Cu Found, ppm	Known Concentration ppm	Source
Coal, NBS	0.92	WA	AA	17± 0.3	~ 18	NBS
Soil						
C-19	1.40	WA	AA	6.3± 0.1		
C-30	1.44	WA	AA	5.7± 0.05		
Material 1577 (Bovine Liver)	0.41	WA	AA	180± 3	193± 10	NBS
Material 1571 (Orchard Leaves)	0.40	WA	AA	12± 0.5	12± 1	NBS
Potatoes, Dried, Mashed (IAEA)	1.08	WA	AA	3.6±0.2	~ 5	SSMS

Table V

Effect of Sample Particle on Scatter of Results

Sample	Spectrometric	Particle mean diameter, μ	Particle mean volume, μ^3[c]	Scatter %
coal	AA	200[a]	4.2×10^6	26.5
crushed coal	AA	60[a]	1.1×10^5	15.6
fly ash	AE	1.67[b]	2.83	6.9
orchard leaves	AA	26[a]	9.2×10^3	6.5
bovine liver	AA	24.8[b]	8.1×10^3	6.7

[a] These are estimated figures obtained from microphotographs of the solid samples.

[b] Obtained by Coulter Counter. The particle diameter range is relatively large, i.e. 1-38μ for bovine liver.

[c] To determine particle volume, a spherical shape was assumed for the solid particles.