

- 9.2.1.5 Add a second portion of 5 ml PDCA-chloroform reagent (7.7.1) and shake vigorously for 2 minutes. Allow the phases to separate and combine the chloroform phase with that obtained in step (9.2.1.4).
- 9.2.1.6 Determine the pH of the aqueous phase and adjust to 4.5.
- 9.2.1.7 Repeat step (9.2.1.4) again combining the solvent extracts.
- 9.2.1.8 Readjust the pH to 5.5, and extract a fourth time. Combine all extracts and evaporate to dryness on a steam bath.
- 9.2.1.9 Hold the beaker at a 45 degree angle, and slowly add 2 ml of conc. distilled nitric acid, rotating the beaker to effect thorough contact of the acid with the residue.
- 9.2.1.10 Place the beaker on a low temperature hotplate or steam bath and evaporate just to dryness.
- 9.2.1.11 Add 2 ml of nitric acid (1:1) to the beaker and heat for 1 minute. Cool, quantitatively transfer the solution to a 10 ml volumetric flask and bring to volume with distilled water. The sample is now ready for analysis.

9.2.2 Prepare a calibration curve by plotting absorbance versus the concentration of the metal standard ( $\mu\text{g}/\text{l}$ ) in the 200 ml extracted standard solution. To calculate sample concentration read the metal value in  $\mu\text{g}/\text{l}$  from the calibration curve or directly from the readout system of the instrument. If dilution of the sample was required use the following equation:

$$\text{mg/l metal in sample} = Z \left( \frac{C + B}{C} \right)$$

where:

Z =  $\mu\text{g}/\text{l}$  of metal in diluted aliquot from calibration curve

B = ml of deionized distilled water used for dilution

C = ml of sample aliquot

9.3 Furnace Procedure: Furnace devices (flameless atomization) are a most useful means of extending detection limits. Because of differences between various makes and models of satisfactory instruments, no detailed operating instructions can be given for each instrument. Instead, the analyst should follow the instructions provided by the manufacturer of his particular instrument and use as a guide the temperature settings and other instrument conditions listed on the individual analysis sheets which are recommended for the Perkin-Elmer HGA-2100. In addition, the following points may be helpful.

9.3.1 With flameless atomization, background correction becomes of high importance especially below 350 nm. This is because certain samples, when atomized, may absorb or scatter light from the hollow cathode lamp. It can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample

beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high.

- 9.3.2 If during atomization all the analyte is not volatilized and removed from the furnace, memory effects will occur. This condition is dependent on several factors such as the volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization and furnace design. If this situation is detected through blank burns, the tube should be cleaned by operating the furnace at full power for the required time period as needed at regular intervals in the analytical scheme.
- 9.3.3 Some of the smaller size furnace devices, or newer furnaces equipped with feedback temperature control (Instrumentation Laboratories MODEL 555, Perkin-Elmer MODELS HGA 2200 and HGA 76B, and Varian MODEL CRA-90) employing faster rates of atomization, can be operated using lower atomization temperatures for shorter time periods than those listed in this manual.
- 9.3.4 Although prior digestion of the sample in many cases is not required providing a representative aliquot of sample can be pipeted into the furnace, it will provide for a more uniform matrix and possibly lessen matrix effects.
- 9.3.5 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.
- 9.3.6 To verify the absence of interference, follow the procedure as given in part 5.2.1.
- 9.3.7 A check standard should be run approximately after every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced. Even though tube life depends on sample matrix and atomization temperature, a conservative estimate would be that a tube will last at least 50 firings. A pyrolytic-coating would extend that estimate by a factor of 3.
- 9.3.8 Calculation—For determination of metal concentration by the furnace: Read the metal value in  $\mu\text{g/l}$  from the calibration curve or directly from the readout system of the instrument.
- 9.3.8.1 If different size furnace injection volumes are used for samples than for standards:

$$\mu\text{g/l of metal in sample} = Z \left( \frac{S}{U} \right)$$

where:

Z =  $\mu\text{g/l}$  of metal read from calibration curve or readout system

S =  $\mu\text{l}$  volume standard injected into furnace for calibration curve

U =  $\mu\text{l}$  volume of sample injected for analysis

9.3.8.2 If dilution of sample was required but sample injection volume same as for standard:

$$\mu\text{g/l of metal in sample} = Z \left( \frac{C + B}{C} \right)$$

where:

Z =  $\mu\text{g/l}$  metal in diluted aliquot from calibration curve

B = ml of deionized distilled water used for dilution

C = ml of sample aliquot

9.3.9 For sample containing particulates:

$$\mu\text{g/l of metal in sample} = Z \left( \frac{V}{C} \right)$$

where:

Z =  $\mu\text{g/l}$  of metal in processed sample from calibration curve (See 9.3.8.1)

V = final volume of processed sample in ml

C = ml of sample aliquot processed

9.3.10 For solid samples: Report all concentrations as mg/kg dry weight

9.3.10.1 Dry sample:

$$\text{mg metal/kg sample} = \frac{\left( \frac{Z}{1,000} \right) V}{D}$$

where:

Z =  $\mu\text{g/l}$  of metal in processed sample from calibration curve (See 9.3.8.1)

V = final volume of processed sample in ml

D = weight of dry sample in grams

9.3.10.2 Wet sample:

$$\text{mg metal/kg sample} = \frac{\left( \frac{Z}{1,000} \right) V}{W \times P}$$

where:

Z =  $\mu\text{g/l}$  of metal in processed sample from calibration curve (See 9.3.8.1)

V = final volume of processed sample in ml

W = weight of wet sample in grams

P = % solids