The method of standard additions can be very useful, however, for the results to be valid the following limitations must be taken into consideration:

a) the absorbance plot of sample and standards must be linear over the concentration range of concern. For best results the slope of the plot should be nearly the same as the slope of the aqueous standard curve. If the slope is significantly different (more than 20%) caution should be exercised.

b) the effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes and the standard addition should respond in a similar manner as the analyte.

c) the determination must be free of spectral interference and corrected for non-specific background interference.

9. General Procedure for Analysis by Atomic Absorption

9.1 Direct Aspiration: Differences between the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for his particular instrument. In general, after choosing the proper hollow cathode lamp for the analysis, the lamp should be allowed to warm up for a minimum of 15 minutes unless operated in a double beam mode. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the hollow cathode current according to the manufactuerer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant, adjust the burner and nebulizer flow rate for maximum percent absorption and stability, and balance the photometer. Run a series of standards of the element under analysis and construct a calibration curve by plotting the concentrations of the standards against the absorbance. For those instruments which read directly in concentration set the curve corrector to read out the proper concentration. Aspirate the samples and determine the concentrations either directly or from the calibration curve. Standards must be run each time a sample or series of samples are run.

9.1.1 Calculation - Direct determination of liquid samples: Read the metal value in mg/1 from the calibration curve or directly from the readout system of the instrument.

9.1.1.1 If dilution of sample was required:

$$\text{mg/1 metal in sample} = A\left(\frac{C + B}{C}\right)$$

where:

A = mg/1 of metal indiluted aliquot from calibration curve
B = ml of deionized distilled water used for dilution
C = ml of sample aliquot

9.1.2 For samples containing particulates:

$$\text{mg/l metal in sample} = A\left(\frac{V}{C}\right)$$

where:

A = mg/1 of metal in processed sample from calibration curve
V = final volume of the processed sample in ml
C = ml of sample aliquot processed

9.1.3 For solid samples: report all concentrations as mg/kg dry weight

9.1.3.1 Dry sample:

$$\text{mg metal/kg sample} = \frac{A \times V}{D}$$

where:

A = mg/1 of metal in processed sample from calibration curve
V = final volume of the processed sample in ml
D = weight of dry sample in grams

9.1.3.2 Wet sample:

$$\text{mg metal/kg sample} = \frac{A \times V}{W \times P}$$

where:

A = mg/1 of metal in processed sample from calibration curve
V = final volume of the processed sample in ml
W = weight of wet sample in grams
P = % solids

9.2 Special Extraction Procedure: When the concentration of the metal is not sufficiently high to determine directly, or when considerable dissolved solids are present in the sample, certain metals may be chelated and extracted with organic solvents. Ammonium pyrrolidine dithiocarbamate (APDC) (see footnote) in methyl isobutyl ketone (MIBK) is widely used for this purpose and is particularly useful for zinc, cadmium, iron, manganese, copper, silver, lead and chromium^{+6}. Tri-valent chromium does not react with APDC unless it has first been converted to the hexavalent form [Atomic Absorption Newsletter *6*, p 128 (1967)]. This procedure is described under method 218.3.

The name ammonium pyrrolidine dithiocarbamate (APDC) is somewhat ambiguous and should more properly be called ammonium, 1-pyrrolidine carbodithioate (APCD), CAS Registry No. 5108-96-3.