

On-Line Dilution for AAS Instruments

Robert O. Miller

Colorado State University

June 10, 2004

NAPT 1st Qtr 2004

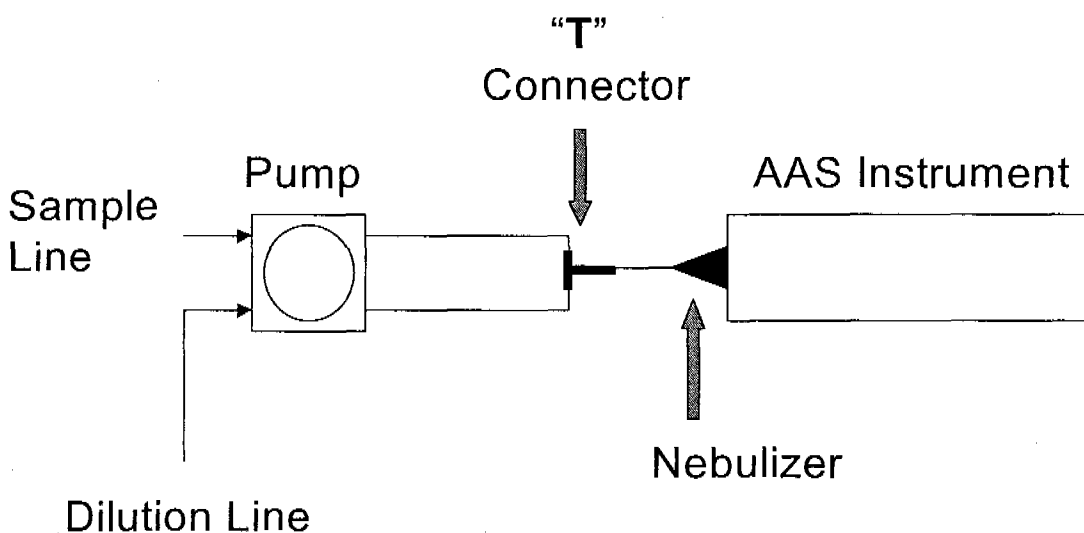
The operation of Atomic Absorption Spectrophotometry (AAS) instruments for the analysis of soil extractable cations (ammonium acetate or Mehlich-3) or plant cations by atomic absorption requires dilution, as element detection is not limiting. Sample dilution ratios vary by AAS instruments, nebulizer design and burner alignment, but typically range from 1:5 to 1:100 ratios. With regard to Ca and Mg the a chemical inference modifier such as Lanthanum is needed to minimize sulfate and phosphate chemical interferences. Generally laboratories conduct the dilution of soil/plant by pipetting out a subsample of extract and dilution with a known volume of the dilutant solution, which in the case is a solution of 5000 mg/L Lanthanum as LaCl_2 in a 2% HNO_3 matrix. Standards and samples are diluted accordingly and the samples are analyzed by an AAS instrument either manually or by the use of autosampler.

This process, of diluting soil/plant extracts and adding matrix modifiers for AAS instruments adds steps to the analytical process, and adds the potential for analytical errors associated with mis calibration of the pipettes and/or the dispenser of the dilution solution. In many instances the labs have replaced the this equipment with auto diluters which improve the process and reduce the error. However, additional time is still needed and there is still the potential an analytical blunder will occur when the wrong sample is diluted or the same sample is mistakenly diluted twice. Further with regard to the addition of a matrix modifier such as Lanthanum large quantities are utilized, despite the fact only 2-3 mL of sample is actually consumed in the process of AAS analysis. Thus several mL of the Lanthanum solution is discarded.

Dr. Robert Carlson, at the University of California at Davis in the 1980s developed an automated online-pump dilution technique for the AAS determination of K, Ca, Mg and Na in soil and plant extracts. The technique can effectively dilute sample extracts real-time while adding matrix modifiers. The technique involves the addition of a 2 channel peristaltic pump positioned directly in front of the AAS nebulizer (and in the case of an instrument with an autosampler directly inline between the autosampler and the AAS instrument) - See Figure 1. By selecting two peristaltic pump tubes (such as those employed on FIA equipments), "T"ing the two lines together and routing the combined solutions directly to the AAS nebulizer, one can dilute samples immediately prior to nebulization in the spray chamber. Selection of pump tubing of different diameters can achieve dilution ratios ranging from 1:1 to 1:80 and combining this with a variable speed peristaltic pump flow rates of 0.25 to 30 mL minute can be achieved.

While Director to the DANR analytical Laboratory at the University California Davis in 1989, and with the help of Dr. Carlson, I instituted this online-pump dilution technique on a Perkin-Elmer model 2380 AAS instrument. The pump was a standard 4-channel peristaltic pump with variable speed capable of 0 - 100 rpm. Pump tubing was selected which provided for a 41X dilution ratio of ammonium acetate extracts. By measuring the AAS normal aspiration rate, it was determined the bead nebulizer optimum flow (maximized) was 5.5 mL per minute. The speed of the 4-channel pump was then adjusted such the flow (from both pump tubes) was 5.5 mL per minute. The base of the T was then connected directly to the nebulizer. The input pump tube with the large diameter line was then attached to a line running to a solution containing 2% HNO_3 , 5000 mg/L Lanthanum and 500 mg/L cesium, while that of the smaller line was used for the standards and sample extracts. Thus, using this set up, soil extracts could be diluted on line with the appropriate matrix modifiers for the determination of K, Ca, Mg and Na by AAS.

Figure 1. Diagram of automated pump dilution for cations by AAS.



Standards were prepared for the AAS, but using concentrations 41X times that typically used, in the case of potassium these were: 4.1, 8.2, 16.4, 32.8 and 49.2 mg/L which resulted in effective concentrations on a soil basis of: 41.0, 82.0, 164, 328 and 492 mg/kg. All other operations of the AAS were conducted according to laboratory standard operating procedures (i.e. wavelengths, slit width, integration time and number of integrations - 3).

Results of the incorporation of the on-line pump dilution of the AAS resulted in improved replicate precision and a slight increase in instrument analysis speed as a result of faster equilibration of the spray chamber with standards and sample solutions. One noted improvement was the decrease in analyte carry-over from a sample containing high concentrations to that of a low. This improvement was attributed to the continuous flushing of the spray chambers by the dilutant solution line between samples. Overall there was an improvement in analysis speed, a reduction in the usage of matrix modifiers, and improvement in analytical precision as a result of the adoption of on-line pump dilution. It was our observation for specific samples, such as water or saturated paste extracts, required different tubing ratios, based on the analyte concentration range observed.

Since our initial adoption of on-line dilution, Byron Vaughan, of MDS Harris Laboratory, Lincoln, Nebraska has further advanced this technique. The original UC Davis work maximized the pump delivery volume (by adjusting the pump speed) to the nebulizer at 5.5 mL per minute, within the optimum range of the AAS instrument manufacturer. Byron's work indicates that the delivery volume can be increased to 20.0 mL/minute for a Perkin-Elmer model 5000 instrument, without any appreciable visible impact on the AAS burner flame or analyte signal stability. By increasing the pump speed the instrument analysis time was substantially reduced, to less than 10 seconds per sample. Further his results of this technique indicated that the coefficient of variation (CV) was lower for the on-line pump dilution technique versus standard lab techniques, which was associated with fewer steps. Overall, this technique can be easily implemented and improve analytical efficiency in the laboratory all the while improving quality.