Factors Affecting the Analytical Performance and Lifetime of Graphite Tube Atomizers

Application Note

Atomic Absorption

Author

B. D. Frary

Introduction

There are, of course, a large number of factors which affect the analytical performance of graphite tube atomizers and the useful working life of individual graphite tubes. The way in which many of these factors impinge on performance and lifetime is either readily apparent or fairly easily ascertained. There are other factors, however, which may not be as well-known and whose mechanism and effect is not quite so readily ascertained. This "At Work" is intended to draw attention to this latter group of factors and suggest ways of minimizing the adverse effects of such factors on analytical response and tube life. Factors are discussed under the following headings:

Electrodes
Tube conditioning
Surface tension and viscosity
Analyte
Matrix
Ashing program
Cooling
Gas
Sampler

Agilent Technologies

Electrodes

When replacing the graphite tube always inspect the contact faces of the electrodes. Usually only a wipe with a laboratory tissue to remove any carbon dust is all that is required. However if signs of pitting are present (which indicates arcing and bad electrical contact) this would result in poor precision and sensitivity and the electrodes would need to be replaced.

Tube Conditioning

Before a new tube is used for analysis it is recommended that a tube clean is performed about 4 times. This ensures that any contamination of the tube during handling is removed. It is also recommended that a tube clean is performed before the start of any analytical determination.

Surface Tension and Viscosity

Generally, the lower the surface tension of the injected solution, the greater the tendency for the solution to creep along the tube. While it is true, for example, that the lower surface tension of organic solvents restricts the volume which can be used, the intrinsic surface tension of particular solutions is not the major problem It is the difference in surface tension between samples and standards, or between samples, which can cause erroneous analytical results and loss of analytical precision. Differences in spreading along the tube may significantly affect the analytical signal because the residence time of analyte atoms within the observation zone will vary depending on how far from the centre of the tube atomization occurs. The partitioned graphite tube (Figure 1) will minimize spreading and thereby improve analytical accuracy and precision, but problems occasioned by differences in surface tension should always be countered by close physical matching of samples and standards.

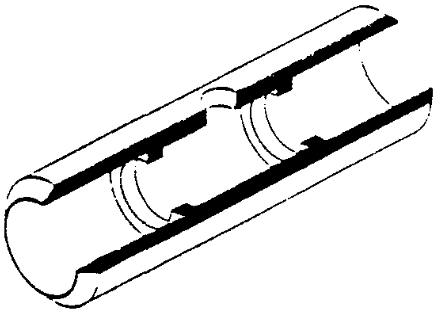
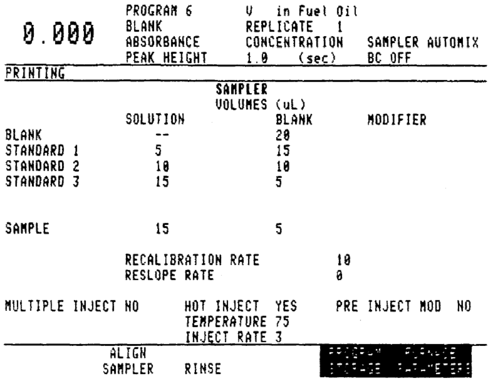


Figure 1. Partition tube.

The spreading of solutions can be countered using the "hot inject" and "injection rate" facilities of the GTA-96 (Figure 2). When "hot inject" is used, the sample is dispensed on to a warm tube and the solvent will evaporate retaining the sample in the centre of the tube. The "hot inject" temperature can be selected in the range 40 to 150 °C. A temperature about half the boiling point of the solvent is initially chosen and is increased in 10 °C steps while investigating the optimum temperature for best precision and sensitivity. The injection rate can be varied between 1 and 45 (arbitrary units). By selecting an injection rate greater than 1 the injection is slowed down thus slowing the formation of the drop and allowing evaporation to proceed.



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          PROGRAM 6        V   in Fuel Oil
  0.000   BLANK            REPLICATE   1
          ABSORBANCE       CONCENTRATION   SAMPLER AUTOMIX
          PEAK HEIGHT      1.0    (sec)    BC OFF
PRINTING
                         SAMPLER
                         VOLUMES (uL)
          SOLUTION               BLANK      MODIFIER
BLANK        --                  20
STANDARD 1   5                   15
STANDARD 2   10                  10
STANDARD 3   15                  5


SAMPLE       15                  5

          RECALIBRATION RATE              10
          RESLOPE RATE                    0

MULTIPLE INJECT NO    HOT INJECT  YES     PRE INJECT MOD  NO
                      TEMPERATURE 75
                      INJECT RATE 3
         ALIGN                         PROGRAM   [illegible]
        SAMPLER    RINSE               STORAGE   PARAMETERS
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Figure 2. Programmable "hot inject" facility.

The viscosity of solutions can have a marked effect on the way in which the solutions are dispensed from the capillary or pipette. The more viscous solutions (oils and some biological materials, for example) tend to cling to the capillary or pipette and a significant proportion will not reach the furnace (Figure 3). Conversely, more mobile solutions may creep over the outside of the capillary or pipette and again a significant proportion will not reach the furnace. Some solutions at high acid concentrations (20% to 50% of acid) are examples of this behaviour. Again, viscosity differences between samples and standards can cause erroneous results and loss of analytical precision, thus physical matching is necessary. The use of standard additions calibration (which may be automatically prepared by the sample dispenser) helps to overcome this.

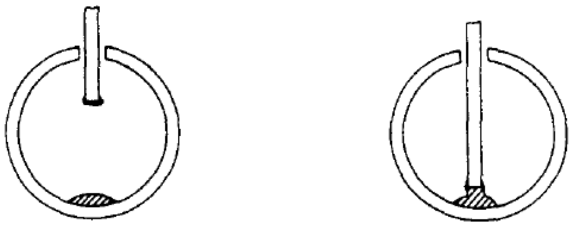
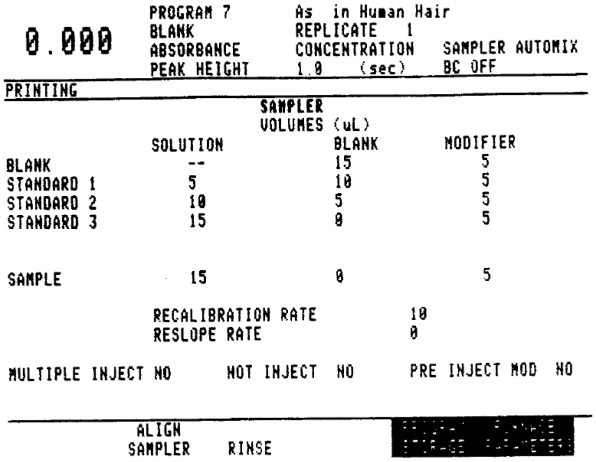


Figure 3. Dispensing of viscous solutions.

Analyte

When determining volatile elements such as arsenic, cadmium, mercury or lead care must be taken to ensure the analyte is not lost during the ashing steps. Volatile elements require the use of a chemical modifier to convert the analyte to a less volatile compound. For example nickel or palladium salts would be used for arsenic; palladium salts for mercury: phosphoric acid for lead and cadmium. A list of modifiers is given in "Analytical Methods for Graphite Tube Atomizers".

A chemical modifier can be added automatically when using the GTA-95 and GTA-96 with a sample dispenser (Figure 4).



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          PROGRAM 7      As  in Human Hair
0.000     BLANK          REPLICATE   1
          ABSORBANCE     CONCENTRATION   SAMPLER AUTOMIX
          PEAK HEIGHT    1.0    (sec)    BC OFF
PRINTING
                        SAMPLER
                        VOLUMES (uL)
          SOLUTION             BLANK       MODIFIER
BLANK        --                15             5
STANDARD 1   5                 10             5
STANDARD 2   10                5              5
STANDARD 3   15                0              5


SAMPLE       15                0              5

          RECALIBRATION RATE         10
          RESLOPE RATE               0

MULTIPLE INJECT NO     HOT INJECT  NO     PRE INJECT MOD  NO

               ALIGN
               SAMPLER    RINSE
```

Figure 4. Programmable use of modifier.

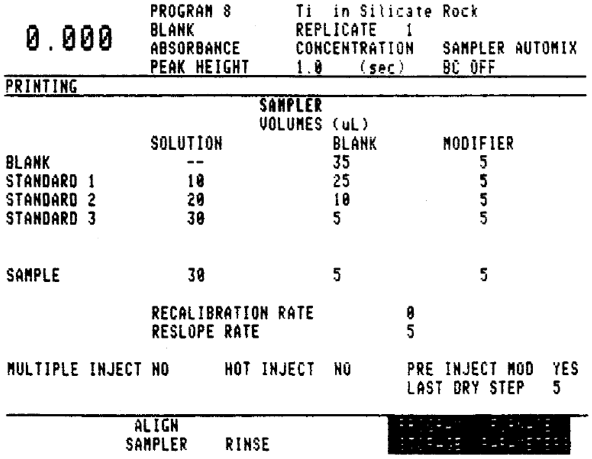
Zirconium and tantalum solutions have been applied to graphite tubes prior to dispensing of the sample (pre¬injection of modifier). Some improvements have been reported; this was attributed to lack of sample contact with the graphite surface due to carbide formation of the zirconium or tantalum.

Some elements such as tungsten will readily form stable carbides with graphite. This will prevent the determination of these elements by furnace AA.

Matrix

With dilute acid as the matrix, graphite tubes can be expected to have a long working life. With seawater matrices containing chemical modifiers (ammonium nitrate), tube life will be considerably reduced because sodium nitrate formed in the mixture will "attack" the pyrolytic graphite. Other matrices may behave similarly. It has been established that reagents such as perchloric acid, perchlorates and sodium nitrate can cause deterioration of the pyrolytic coating, and high concentrations of such reagents will shorten tube life considerably. Other powerful oxidizing agents may have a similar effect.

High concentrations of nitric acid do not appear to seriously affect the pyrolytic coating, nor do high concentrations of sodium chloride. Nevertheless, it is desirable to keep the concentrations of acids to a minimum where possible. Some matrices by diffusing through the surface can cause delamination of the pyrolytic surface and thus cause early failure of the tube. It may be possible to avoid this by using a modifier which will coat the tube and prevent the matrix attacking the pyrolytic graphite crystal structure. A facility is provided with the GTA-96 and sampler which allows pre-injection of modifier for this purpose (Figure 5). Tantalum or zirconium salts may be used.



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          PROGRAM 8      Ti  in Silicate Rock
0.000     BLANK          REPLICATE   1
          ABSORBANCE     CONCENTRATION   SAMPLER AUTOMIX
          PEAK HEIGHT    1.0    (sec)    BC OFF
PRINTING
                        SAMPLER
                        VOLUMES (uL)
          SOLUTION             BLANK       MODIFIER
BLANK        --                35             5
STANDARD 1   10                25             5
STANDARD 2   20                10             5
STANDARD 3   30                5              5


SAMPLE       30                5              5

          RECALIBRATION RATE         0
          RESLOPE RATE               5

MULTIPLE INJECT NO     HOT INJECT  NO     PRE INJECT MOD  YES
                                          LAST DRY STEP   5

               ALIGN
               SAMPLER    RINSE
```

Figure 5. Programmable blank to dispense to constant volume.

Ashing Program

Some analytical methods may involve an air or oxygen ash to remove excess amounts of carbon present in samples such as blood. The recommended maximum ashing temperature for an air or oxygen ash is 450 °C, but it must be remembered that air or oxygen ashing will reduce tube life.

After air or oxygen ashing at 450 °C, inert gas should always be switched on for at least 5 seconds to flush out air or oxygen before going to a higher ashing temperature or to the atomization stage. If inert gas is not introduced in this way, the analytical performance will be degraded comparatively quickly, and tube life will be considerably shortened.

When establishing ashing temperatures, particular care should be taken to ensure that analyte is not lost during this stage of the furnace program. The best way to examine this aspect is to construct a graph of absorbance against ash temperature (Figure 6) as discussed in the "Analytical Methodology" Chapter and the "Development of Analytical Programs" Chapter of Varian's "Analytical Methods for Graphite Tube Atomizers".

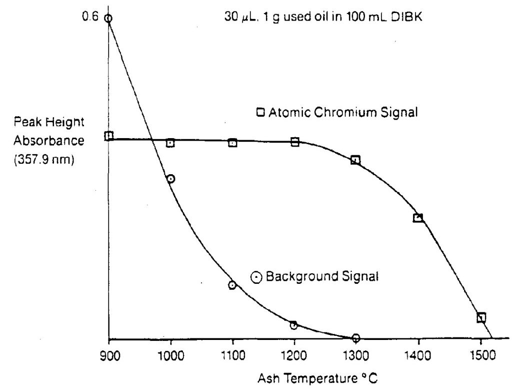

Figure 6. Ashing versus absorbance graph.

Cooling

A built-in 20 second cool down step is applied at the end of the furnace program. This is sufficient time to allow the tube to cool down to a reproducible injection temperature from atomization temperatures. When platforms are used a cool down step should be added to the furnace program. This ensures a reproducible injection temperature and thus optimum precision is obtained.

The GTA-95 and GTA-96 both monitor the cooling water temperature and operation will be automatically stopped if this is outside the range 1 to 40 °C.

Gas

It is strongly recommended that argon be used for all determinations. If nitrogen is used for any reason, it should be the highest purity available. Note, however, that even the purest commercially available nitrogen may contain residual oxygen which can degrade analytical sensitivity by promoting the formation of analyte oxides immediately after atomization, and tube life will be shortened. Argon should always be used in preference to nitrogen at atomization temperatures above 2500 °C. Under these conditions, nitrogen will "attack" the graphite and form CN species which will reduce tube life and by combining with the analyte will suppress the absorbance. CN emission bands will add to the difficulty of determining some elements whose resonance lines are close to those of the CN bands.

The temperature program should include a gas stop step before the atomization stage, 2 seconds being sufficient to allow the gas flow to decay to zero. Setting longer times than necessary for this and the atomization stage with zero gas flow will shorten tube life.

Sampler

Before starting the analytical program, always inspect the syringe to ensure that there are no gas bubbles in the system. Any bubbles in the system will cause dispensing errors which in turn will lead to erroneous results and loss of analytical precision. If necessary, bleed the syringe as described in the installation instructions given in the Operation Manual.

It is recommended that the system is programmed to work to constant volume. Blank solution should be added to ensure each solution dispensed is the same volume (Figure 2). This has several advantages:

1. The blank solution is the last solution dispensed and will flush out any traces of standard or sample solution that may be left in the capillary.
2. The volume dispensed is the same for all solutions thus each will cover the same area of the tube surface and be subject to the same thermal environment.
3. The height of the capillary tip is set for the one volume dispensed and no compromise is required.

This procedure enables the optimum precision and accuracy to be achieved. After several days use a black film of graphite may appear on the outside of the capillary. This can affect the accuracy of dispensing and should be carefully wiped off with a tissue. Capillary alignment should be checked before use.

The recommended rinse solution contains 0.005% Triton X-100 and 0.01% nitric acid by volume. When using organic solutions the rinse vessel may contain the organic solvent used or an aqueous solution of Triton X-100.

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