



Analysis of High Solids Solutions by Flame Atomic Absorption

Application Note

Atomic Absorption

Author

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Introduction

The analysis of solutions containing appreciable amounts of dissolved solids by flame atomic absorption requires careful consideration of the solution chemistry and sample preparation as well as an informed choice of instrumental operating conditions in order to obtain reliable results. A common problem is the physical obstruction of parts of the flame atomizer by salt accumulation which leads to a drift in calibration and consequent inaccuracies in the analysis.

Solutions having a total dissolved solids level in excess of around 1% warrant consideration of the factors discussed in this paper. The magnitude and speed of the effect will depend greatly on the type of salt—for example a 50% solution of ammonium acetate can be aspirated continuously without effect whereas a 5% solution of sodium acetate will induce significant effects within minutes.

The interfering effect of excess levels of other components on the atomization process in the flame is a further compelling reason for minimizing the level of dissolved solids.



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Salt Deposition

In a flame atomization system the sample solution is converted into an aerosol consisting of small droplets dispersed in the primary oxidant gas. This aerosol is mixed with fuel gas (and sometimes auxiliary oxidant gas) and the mixture passes through the burner slot into the flame. During this process evaporation of the solution occurs and consequently the concentration of dissolved solids in the aerosol droplets increases. If the concentration exceeds the saturation point dissolved solids will be precipitated from solution and can accumulate in the flame atomizer.

Such accumulation can result in deterioration of the analytical performance of the atomizer. There are three places in the atomizer where conditions favor evaporation of solution and where accumulation of precipitated solids occur:

The Nebulizer

In the initial formation of aerosol by the nebulizer the solution is dispersed by a stream of dry oxidant gas. This results in evaporation and cooling, both processes favorable to the precipitation of salts from solution. If the concentration of dissolved solids is such that the saturation point can be exceeded by the evaporation and cooling occurring in the nebulizer, salts will be deposited and the performance of the nebulizer will deteriorate. The Agilent fixed uptake rate nebulizer design minimizes this salt build-up and should be used in preference to the adjustable nebulizer.

Nebulizing distilled or deionised water between samples helps to remove any material accumulated in regions around the nebulizer venturi reached by the spray. In some instances, however, particles accumulate behind the venturi where they cannot be dislodged by nebulizing water. Material lodged behind the venturi can cause corrosion of the internal components of the nebulizer. In order to prevent this it is good practice to clean the nebulizer at the end of each day when high solids solutions have been nebulized. Turn off the flame, remove the bung from the spray chamber and remove the nebulizer from the bung. Soak the nebulizer in hot water and detergent and rinse with distilled water. From time to time it may be necessary to disassemble the nebulizer for more thorough cleaning [1].

The Fuel and Auxiliary Oxidant Inlet

At this point the aerosol droplets encounter another stream of dry gas. Droplets adhering to the edges of the fuel inlet can evaporate to the saturation point, depositing solid material which then forms a nucleus for further droplet accumulation and solids deposition. Solids can accumulate to such an extent that the fuel inlet becomes completely obstructed and the flame is extinguished. Before this happens the partially clogged inlet typically results in the absorbance signal becoming very noisy. Serious drift in the absorbance signal often occurs as well.

The Burner Slot

During the passage of the aerosol through the burner slot, droplets can adhere to the walls of the slot and evaporate, depositing solid material. This material forms the nucleus for further deposition and eventually the burner slot can become clogged with accumulated solids. Clogging of the burner slot becomes evident to the operator by the appearance of a ragged edge to the inner cone of the flame, followed by isolated "nicks" in the inner cone which develop into divisions extending through the entire flame. Drift in absorbance occurs soon after the first appearance of these effects. As the clogging process proceeds, the pressure in the spray chamber increases, resulting in an increase in gas velocity through the burner slot.

With the air-acetylene flame this increase in gas velocity eventually exceeds the burning velocity of the flame, so the flame lifts off the burner and extinguishes. Because of the higher burning velocity of the nitrous oxide flame the slot can become very severely clogged without the flame lifting off. In extreme cases the pressure in the spray chamber can increase to such an extent that the liquid seal in the drain trap is breached.

Clogging of the burner slot can be reduced by the use of an appropriately designed burner. The extent to which aerosol droplets adhere to the walls of the burner slot is greatly influenced by the slot geometry. The shape of the lower part of the slot where the aerosol enters is especially critical. The Agilent Mark V burners have been designed specifically to provide a slot geometry favoring smooth passage of aerosol from the burner cavity into the flame. With these burners aerosol adhesion to the walls of the slot and consequent solids accumulation is significantly reduced.

Another important factor affecting the deposition of solids in the burner slot is the surface finish. Scratches or imperfections in the slot walls can act as nuclei for the accumulation of aerosol droplets and greatly increase the rate of blockage. For this reason it is necessary to take great care not to scratch the slot walls when cleaning the burner.

Dirt in the burner slot has the same effect as poor surface finish, so regular cleaning of the burner slot is essential. (A procedure is given below.)

Agilent supplies two different burners of the Mark V design, an air-acetylene burner and a nitrous oxide-acetylene burner. The nitrous oxide burner can be used with an air-acetylene flame, which allows this burner to be used as a universal burner. Because of the smaller dimensions of the burner slot on the nitrous oxide-acetylene burner it is significantly more susceptible to solids accumulation than the air-acetylene burner. It is therefore advantageous to use the air-acetylene burner whenever high solids solutions have to be analyzed using the air-acetylene flame. The air-acetylene burner cannot, of course, be used for the nitrous oxide-acetylene flame. The burning velocity of nitrous oxide-acetylene flames is much faster than that of air-acetylene flames and an attempt to use the larger slot air-acetylene burner with nitrous oxide could easily result in an explosion. All current Agilent atomic absorption instruments are fitted with interlocks which inhibit the use of nitrous oxide with the air-acetylene burner.

Sample Preparation

Interruptions of analytical work resulting from accumulation of solids in the flame atomizer are obviously inconvenient to the analyst. They can, however, be minimized by taking appropriate precautions during the sample preparation procedure. Some guidelines which will be of assistance in this area are as follows:

- Keep the total concentration of dissolved solids as low as possible. The benefits of this are twofold. Firstly, the lower the concentration the less likely it is that the saturation point will be reached, thus minimizing the risk of clogging the nebulizer. Secondly, the lower the concentration the less material will be deposited by the evaporation of adhering droplets in the burner slot, so the time required for significant obstruction of the slot to occur will be greatly increased.

Figure 1 shows that the time required to block the burner is to a good approximation inversely proportional to the salt concentration. It is evident that reducing the concen-

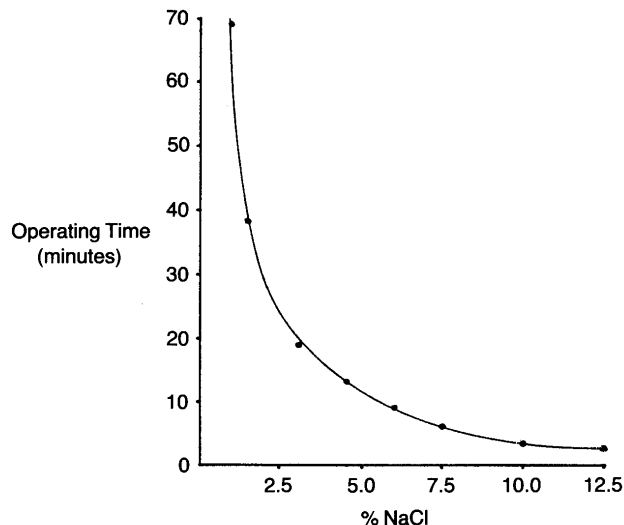


Figure 1. Operating time as a function of sodium chloride concentration. **

tration of dissolved solids can have a very significant effect on the time available for analysis between cleaning the burner.

Very frequently burner clogging problems arise not from the sample itself but from materials used to take the sample into solution. Fusions naturally introduce more solids into the final solutions than acid digestions. When a fusion must be used it is obviously preferable for optimum instrument performance to use the lowest possible ratio of flux to sample. Time spent during method development establishing minimum flux to sample ratios will be more than compensated for by reduced downtime during atomic absorption analysis of the samples. Once minimum flux to sample ratios have been established, the quantity of sample and flux used for each fusion should be kept as small as possible.

- Take advantage of the absorbance expansion facilities of modern instrumentation. When working with high solids solutions it may be preferable to adjust the sample preparation procedure to reduce the solids concentration and compensate for any loss in analytical sensitivity by expansion.
- Adjust the sample preparation procedure to obtain the least troublesome matrix. Often it is possible to select which salts will be present in a sample solution. For instance sodium peroxide fusions could be dissolved in hydrochloric acid, yielding a solution of sodium chloride, or in nitric acid to yield sodium nitrate. These two salts behave very differently in the flame atomizer as shown in Figure 2. The solution of sodium chloride blocked the

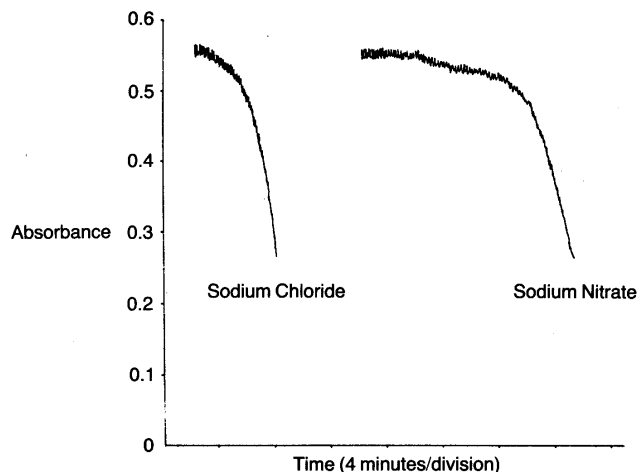


Figure 2. Copper signal as a function of time in 1.28 M sodium solutions. **

burner slot very rapidly, while the equivalent sodium nitrate solution took much longer to have any effect.

When dissolving fusions there is no benefit in using large excesses of acid. Indeed, excessive acid can increase problems with burner clogging because of reduced solubilities of matrix salts (Table 1).

Table 1. Effect of Hydrochloric Acid Concentration on Burner Blocking Time with 7.5% NaCl Solution. Results are the Mean of Three Measurements**

Solution	Operating time
5 ppm Cu + 7.5% NaCl + 0.1 M HCl	6.1 ± 0.7
5 ppm Cu + 7.5% NaCl + 1 M HCl	4.1 ± 0.3

Glass Bead Adjustment

Once these precautions have been observed, any remaining problems can be minimized by the simple procedure of readjusting the position of the glass impact bead to reduce the amount of aerosol produced from a given uptake rate of solution. This naturally lowers the instrument response as well as improving the solids handling capability, but in many cases this is an acceptable trade. Figure 3 gives an example of the effect of moving the bead. The magnitude of the improvement in blocking time will depend on the particular salt involved as well as on the gas flow rates being used.

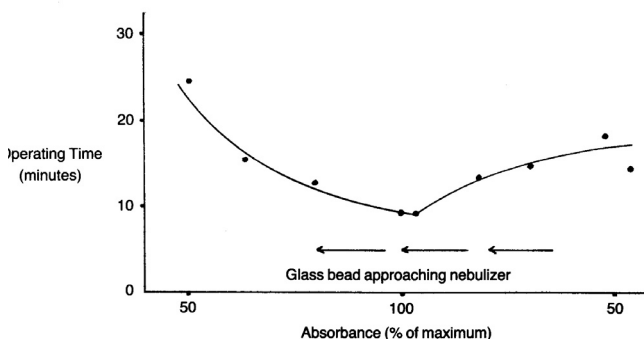


Figure 3. Operating time as a function of the glass bead position. Test solution was 5 mg/L Cu with 7.5% NaCl in 0.1 M HCl. **

** For purposes of illustration all figures in this report were obtained using an air-acetylene flame on a Varian Mark V nitrous oxide-acetylene burner. Longer operating times are achieved when the air-acetylene burner is used, where the limiting factor is likely to be the blockage of the fuel inlet. The instrument used was a Varian AA-975, with the standard Mark V spray chamber and a Varian fixed nebulizer. Operating conditions were adjusted to obtain maximum absorbance for copper in the air-acetylene flame. The burner was considered to be blocked when the absorbance of a solution aspirated continuously had dropped to 50% of its initial value.

To adjust the bead position, proceed as follows:

1. Turn off the flame.
2. Remove the nebulizer bung assembly.
3. Loosen the screw securing the glass bead in the mounting block.
4. Gently twist the bead to ensure that the screw is no longer gripping the bead.
5. Turn the adjusting screw, noting how the mounting block moves.
6. Turn the adjusting screw clockwise until the mounting block is located at the limit of its travel towards the head of the adjusting screw.
7. With the mounting block in this position carefully adjust the position of the bead in the mounting block so that a piece of thin paper just fits between the bead and the nebulizer.
8. Tighten the screw securing the bead in the mounting block.
9. Operate the adjusting screw, observing that the bead moves away from the nebulizer as the screw is turned anticlockwise. Leave the bead at the maximum distance from the nebulizer.
10. Mount the bung in the spray chamber. Set up the instrument for the measurement of copper in the air-acetylene flame and nebulize a convenient copper standard (2-5 mg L⁻¹). Adjust the burner to the position of maximum absorbance, then carefully turn the bead adjusting screw until the absorbance reaches a maximum.
11. When the point of maximum absorbance has been reached, turn the adjusting screw clockwise until the absorbance drops to 50% of its maximum value.
12. The bead position has now been set to a position indicated by the arrow on Figure 3, and significant improvements in the solids handling characteristics of the flame atomizer will result.

Gas Flows

Increased gas flows through the spray chamber can accelerate the salt deposition processes in the burner slot and in the fuel/auxiliary oxidant inlet. For this reason auxiliary oxidant should, in general, not be used when high solids solutions are analyzed. Set the oxidant flow to its minimum value and adjust the fuel to obtain the appropriate flame conditions.

Standards

Whenever high solids samples are analyzed it is important that the composition of the standards should be as close as possible to that of the samples. If this precaution is ignored serious errors are to be expected, as chemical and physical interferences are almost certain to occur.

Burner Cleaning

When high solids solutions are analyzed, cleaning of the burner slot will be required from time to time, as indicated by the appearance of the flame. To clean the burner, turn off the flame, remove the burner (use heat resisting gloves) and remove accumulated solids by washing the burner under the tap. Carefully pass the metal cleaning strip through the slot, wash the burner again and rinse with distilled water. Dry with compressed air. Every time it is necessary to clean the burner, the spray chamber should also be removed and cleaned. Give the spray chamber a good rinse under the tap and dry the gas inlets with compressed air.

References

1. Nebulizers for Atomic Absorption Spectrophotometers—Operation Manual, Varian Techtron Pty. Limited, Mulgrave, Australia, Publication No. 85-100360-00, March 1980.

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