

Matrix modifier for furnace AA

A matrix modifier is occasionally used with atomic absorption spectrophotometry. Matrix modifiers are also known as interference suppressants or chemical modifiers. Matrix modifier is a generic term for a

substance added to achieve various effects, such as enhanced sensitivity or repeatability. This Application News discusses matrix modifiers for furnace AA.

. Interference

Interference is one of the problems that must be considered in disturbance atomic absorption spectrophotometry. Interference can be described as disturbance during measurement due to coexisting substances in the sample. Atomic absorption spectrophotometry is a method of relative analysis that creates calibration curves from standards of known concentration, then uses these calibration curves to measure a sample of unknown concentration. Consequently, differences in composition of the standard and sample will result in inaccurate measured concentration values. This phenomenon is generally called "interference." The typical types of interference are listed below.

- ① Physical interference
Interference due to viscosity differences between the standard and sample.
- ② Background interference
Interference due to absorption and scattering from coexisting molecules in the sample.
- ③ Chemical interference
Interference due to bonds between the coexisting substances and (released) elements in the sample.
- ④ Ionization interference
Interference due to the different equilibrium states of the atoms/ions in the sample

. Matrix modifiers

Several parameters, such as wavelength and lamp current, must be set before atomic absorption spectrophotometry analysis. Only some of parameters directly affect the measured results. For furnace atomic absorption spectrophotometry, these parameters are the graphite tube type and the heating conditions. Changing these parameters to determine the conditions of minimum interference is an unavoidable task for improving the quality of the measured values. However, adjustment of the equipment is not sufficient to overcome this problem for some samples, and in these cases matrix modifiers are effective. The effects of matrix modifiers are as follows:

- ① masking interfering components;
- ② eliminating interfering components;
- ③ restricting vaporization of measured elements.

The effect ① is mainly used for flame AA. Changing the form of coexisting substances in the flame such that they cannot disrupt the measured elements and eliminates interference.

The effects ② and ③ are used for furnace AA. Furnace AA atomizes the sample through drying and pyrolysis. Pyrolysis is a stage to eliminate interfering components, so in a sense, the higher the furnace temperature setting the better. However, increasing the temperature also increases the danger of vaporizing the measured elements themselves. This effect is particularly strong for elements with a low melting point, such as As, Cd, or Pb. As low-melting-point elements are easily vaporized, a high pyrolysis temperature setting reduces sensitivity and hinders reproducibility. Conversely, a temperature set low enough to prevent vaporization of the measured elements is insufficient to fully eliminate the interfering components, so that interference occurs during atomization. The above explanation suggests two methods for restricting interference. One method (② above) is to convert the interfering components into a more easily vaporizable form, allowing easy elimination at lower pyrolysis temperatures. The other method (③ above) is to convert the measured elements into a less easily vaporized form, allowing the pyrolysis temperature setting to be increased, resulting in easy elimination of the interfering components.

The type ② of modifier is also called a sublimation agent. In furnace AA, sodium chloride is a cause of background interference and is also a low-boiling-point chloride that reacts with the measured element. Ammonium nitrate can be used to eliminate sodium chloride. The sodium chloride reacts with the ammonium nitrate to form ammonium chloride and sodium nitrate, which both vaporize at low temperature and are easily eliminated.

The type ③ of modifier is also called a stabilizer. Alloying is one method of converting the measured element into a less volatile form. The platinum group modifiers are used for alloying. Palladium and other platinum-group elements are widely used as catalysts but their properties can also be exploited as additives

to promote alloying in furnace AA.

Table 1 shows a list of typical matrix modifiers used for furnace AA. As an example of the effect of modifier addition, Fig. 1 shows a comparison of the peak profiles

of Cd (2ppb Cd) without additive and of Cd with a Pd additive (2ppb Cd + 100ppm Pd).

Table 1 Table 1 List of matrix modifiers

Ag	ascorbic acid, Cu, Mg+Pd, Pd	Mg	ammonium nitrate
Al	ammonium nitrate, magnesium nitrate, Mg+Pd, sulfuric acid	Mn	ammonium nitrate, ascorbic acid, magnesium nitrate, Mg+Pd
As	Cu, magnesium nitrate, Mg+Ni, Mg+Pd, Ni, Pd, Rh	Mo	ascorbic acid, Ca, magnesium nitrate, Pd
Au	Mg+Pd, Pd	Ni	ammonium nitrate, magnesium nitrate, ammonium phosphate
B	calcium chloride, Ca+Mg, magnesium nitrate	Pb	ammonium nitrate, magnesium nitrate, Mg+Pd, Pd, ammonium phosphate
Be	magnesium nitrate	Pd	magnesium nitrate
Bi	ammonia, Cu, Mg+Pd, Ni, Pd	Sb	Sb Mg+Pd, Ni, Pd
Cd	ammonium nitrate, ascorbic acid, Pd, ammonium phosphate	Se	magnesium nitrate, Mg+Ni, Mg+Pd, Ni, Ni+Pd. Pd, Rh
Co	ammonium nitrate, ascorbic acid, magnesium nitrate, Pd	Si	ammonium nitrate, Ca, Pd
Cr	ascorbic acid, magnesium nitrate, Pd	Sn	ammonium nitrate, ascorbic acid, Mg+Pd, Pd
Cs	potassium chloride, potassium nitrate	Te	Mg+Pd, Ni, Ni+Pd, Pd
Cu	ammonium nitrate, Mg+Pd, Pd	Tl	Mg+Pd, Ni, Pd
Fe	ammonium nitrate, magnesium nitrate, Mg+Pd	V	ascorbic acid, magnesium nitrate
Li	ammonium nitrate, sulfuric acid	Zn	ascorbic acid, magnesium nitrate

. Notices when using matrix modifiers

The amount of modifier used differs according to the modifier type, but several ten ppm to several hundred ppm is the amount generally used for furnace AA. We have to take notice of the following points when using modifiers:

- ① contamination by the modifier;
- ② limits on modifier effect;
- ③ reverse effects from modifier addition,

Point ① is related to the amount and purity of modifier added. The modifier itself may contain the measured element. A check must be made with a sample blank when using a modifier.

For point ②, if the addition of a modifier reveals a previously unseen peak, the degree to which interference has been eliminated remains unclear. If an additive recovery test results in unsatisfactory recovery rates, consider changing the modifier type or volume, or using an extra standard additive method.

The point ③ can occur and care is required. This refers to the possibility of reduced volatilization of the interfering components resulting from modifier addition, such that background interference increases. Also, excessive amounts of modifier can hinder atomization of the measured element, such that modifier addition has a negative effect.

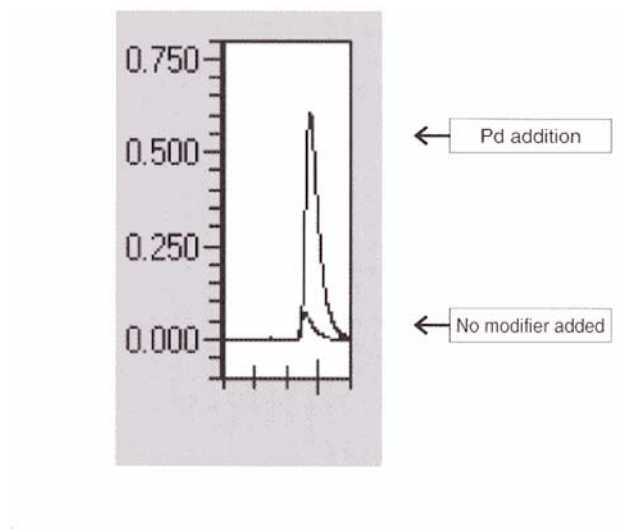


Fig.1 Measurement of Cd with a matrix modifier



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