Direct Determination of Phosphorus in Organic Matrices by Atomic Absorption

Application Note

Atomic Absorption

Author

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Introduction

Zinc dithiophosphate is one form of phosphorus added to petroleum products. The control of its concentration and that of other forms of phosphorus is important in quality control of finished products and also because of the deleterious effects of phosphorus to the environment. In Canada, the maximum concentration of phosphorus in oil will soon be regulated at 100 µg/mL. With the increasing interest in phosphorus, analysts are looking fore fast, reliable method of determining its concentration.

As discussed in AA At Work Number 19, "Direct Determination of Phosphorus in Aqueous Matrices by Atomic Absorption", phosphorus can be determined directly by flame AA. Samples should have a viscosity appropriate for aspiration and dissolved solids content less than 7% to eliminate blockage of the nebulizer and build-up in or on the burner head Since organic solvents used for AA analysis are combustible, an adjustable nebulizer should be used to reduce uptake rate, ensuring good flame stoichiometry.

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Results — Flame AA

Figure 1 shows the phosphorus calibration curve for oil analysis by flame AA. Parameters used are shown in Table 1.

Table 1.

AA-875 Instrument Parameters:

Wavelength	213.6 nm
SBW	0.2 nm
Background correction	No
Electrodeless Discharge Lamp	
EDL power	6 watts
AA lamp current	7 mA
Flame	N_2O-Acetylene
Stoichiometry	A lean flame with water being aspirated

Note: Burner position was adjusted so that the light path was one centimeter above the burner. Nebulizer uptake rate was approximately 3 mL/min.

Triphenyl phospene was used for the standards in Figure 1. Standards were made with a 25% (v/v) level of viscous neutral oil in xylene diluent. Samples were prepared in the same way. MIBK diluent caused a 25–30% loss in sensitivity for phosphorus.

Organic standards produce absorbances twice those of aqueous standards of the same phosphorus concentration. The characteristic concentration (sensitivity) and detection limit for phosphorus in organic matrices is 64 µg/mL and 21 µg/mL respectively. Figure 2 shows a bar graph presentation of the detection limit study. A 224 µg/mL P standard was used with 10X scale expansion and 10 second integration readings. The instrument was sewed with an air blank and then the organic solvent was aspirated as a solvent blank.

Results — Furnace AA

It is recommended that the carbon rod be used for phosphorus concentrations below 200 µg/mL. As discussed in the previous paper [1], the ability to determine phosphorus on the carbon rod depends upon the use of a stabilizer. In the past, lanthanum was suggested as the best stabilizer. However, lanthanum has a tendency to degrade the graphite tubes, and it also has a high boiling point which causes a build-up of the lanthanum, eventually producing a loss in sensitivity. Lastly, lanthanum is expensive. Nickel has been found to be a superior stabilizer. Nickel gives improved sensitivity and longer tube life. The source of nickel needs to be soluble in the organic diluents used. All organo-nickel compounds tested were acceptable. One of the compounds used was a nickel sulphonate salt with a molecular weight of 500 obtained from Conostan. As in the study on aqueous solutions [1], different concentrations were checked and the best overall performance was found using 2000 µg/mL Ni for stabilization.

Bar Graph Group #	Conc. of P	Mean Int. ABS.	% RSD Int. ABS.
1	1000	.068	0.8
2	2000	.137	0.4
3	3000	.206	0.2
4	8000	.474	1.0

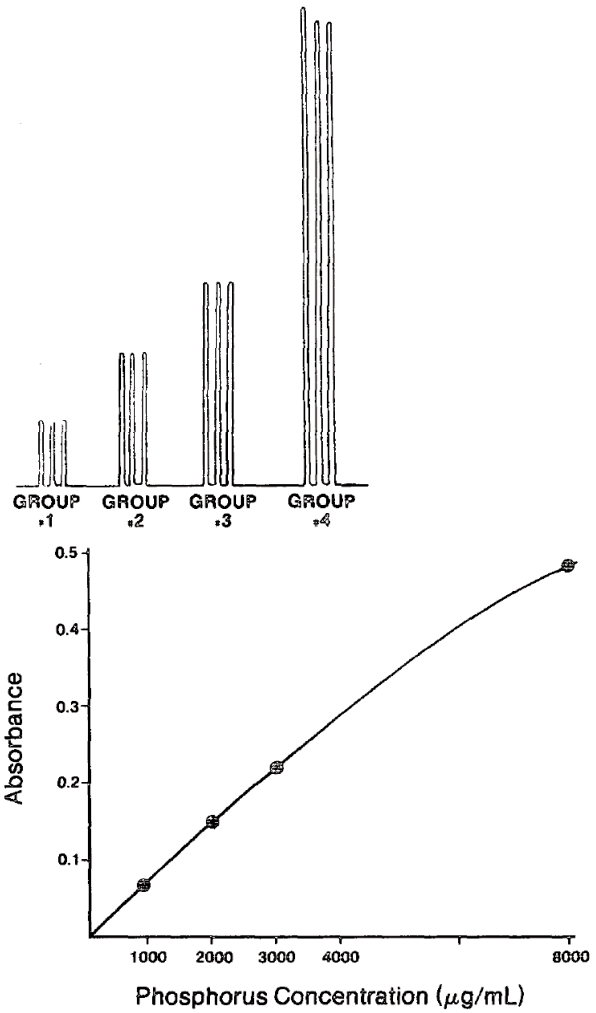

Figure 1. Flame determination of phosphorus in organic matrices.

Standards were made with a 25% (v/v) level of viscous neutral oil in a deodorized kerosene diluent. Samples were diluted in the same manner to give the same viscosity properties as the standards.

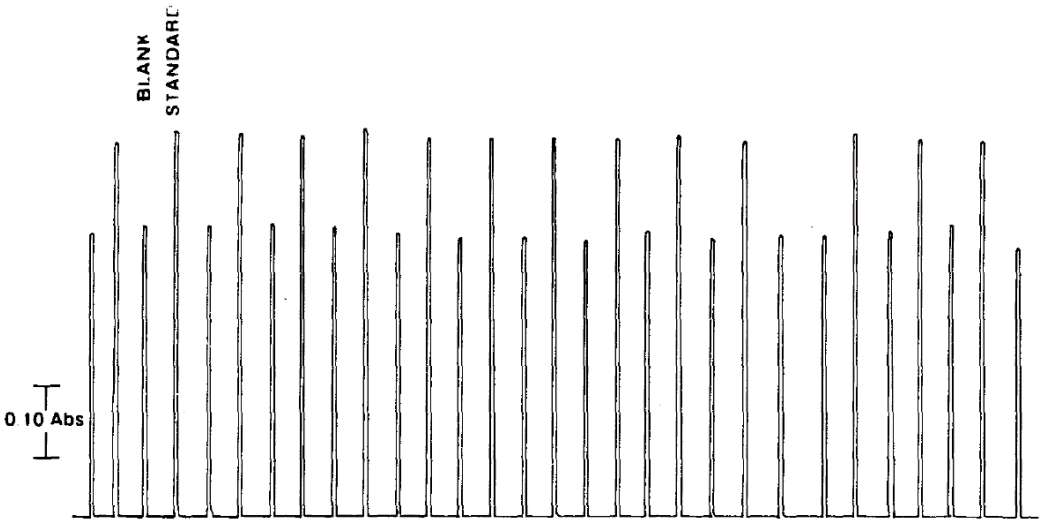

Figure 2. Detection limit for phosphorus in oil–Flame AA.

Results for the determination of phosphorus in oil are shown in Figure 3. At phosphorus concentrations greater than 200 µg/mL, the calibration curve begins to flatten dramatically. Apparently, the nickel concentration is no longer large enough to stabilize the phosphorus. However, larger nickel concentrations should not be used because reproducibility and tube life degrade rapidly. Phosphorus concentrations should not exceed 200 µg/mL for CRA determinations. If phosphorus concentrations are less than 50 µg/mL, 1000 µg/mL Ni should be used for stabilization.

Reproducibility of the CRA method is shown in Figure 4. Twenty replicates of 150 µg/mL P gave a mean absorbance of 0.456. The relative standard deviation was 3.33%. Routine precisions for oil samples normally range from 2 to 6% RSD. Parameters used for the analysis are shown in Table 2.

Table 2.

AA-875 Instrument Parameters:	
Wavelength	213.6 nm
SBW	0.2 nm
Background correction	on
Electrodeless Discharge Lamp (EDL)	
EDL power	6 watts
AA lamp current	7 mA
CRA-90 Parameters:	
10 µL injection	
Threaded tubes	
Dry	200 ° for 45 seconds
Ash	1100 ° for 15 seconds
Atomize	2500 °: Hold: ¾ second
Ramp	800 °C/sec
Sheath gas	Argon*
Stabilizer	0.2% Ni

*N_2 may be used with a slight loss in sensitivity

Figure 5 shows a graphics printout from the HP-85 computer for AA. It shows that some background is present which can be easily corrected for by the instrument. By the time the carbon rod reaches the programmed atomize temperature, all of the phosphorus has been atomized. The high atomization temperature is necessary to vaporize all the stabilizer.

Conclusion

Phosphorus can be determined in organic matrices directly by AA. The sample preparation is normally very simple and the normal working range for flame determinations is 200–8000 µg/mL P. For phosphorus concentrations below 200 µg/mL, the carbon rod should be used, and a stabilizer (2000 µg/mL Ni) must be added to all solutions. Phosphorus concentrations determined should not exceed 200 µg/mL due to flattening of the calibration curve. For the analyst faced with the task of determining phosphorus in organic matrices, atomic absorption provides a quick, reliable means of analysis.

References

1. W. G. Hobbins, “Direct Determination of Phosphorus in Aqueous Matrices by Atomic Absorption”, Varian Instruments at Work, Number AA-19, December 1981.

Conc. of P	Mean Pk. Height	% RSD Pk. Ht.	Mean Pk. Area	% RSD Peak Area
50	.249	6.0%	.088	8.1%
150	.481	1.0%	.178	9.4%
250	.566	2.6%	.231	2.5%

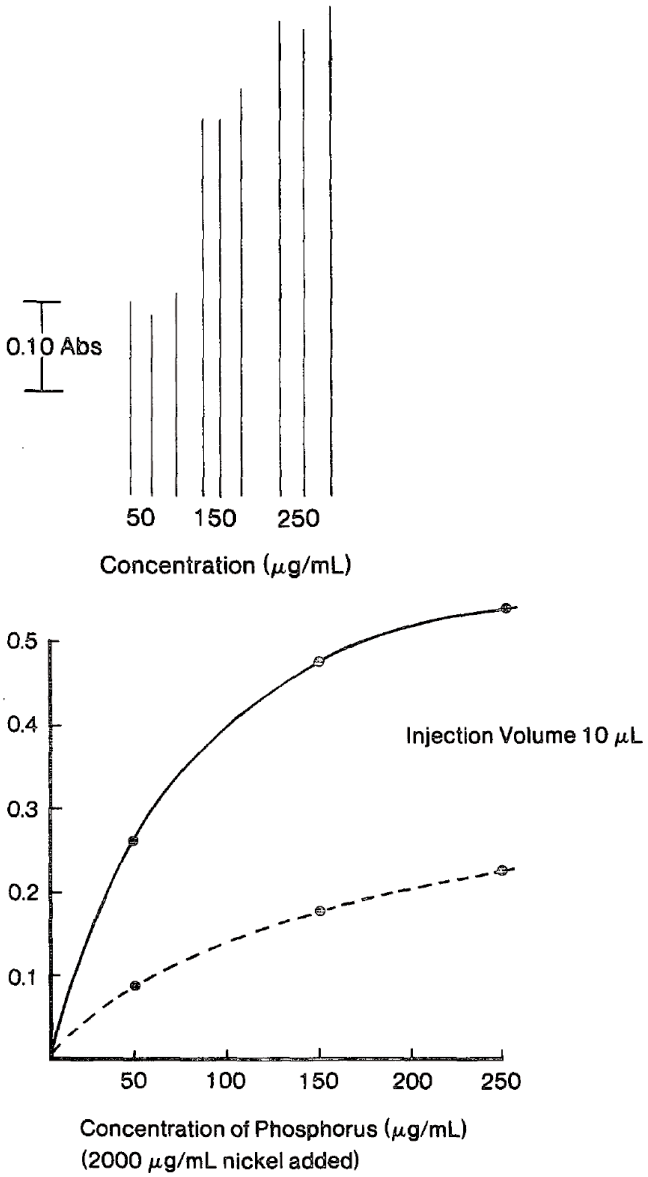

Figure 3. CRA-90 Determination of phosphorus in oil.

150 μg/mL phosphorus
2000 μg/mL nickel stabilizer
Injection volume 10 μL
Mean 0.456
Precision 3.33% RSD

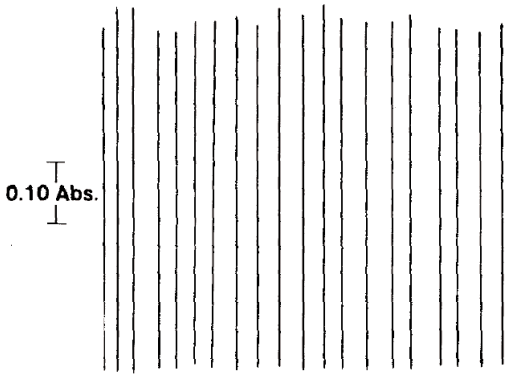

Figure 4. Reproducibility for phosphorus in oil CRA-90 Carbon rod atomizer.

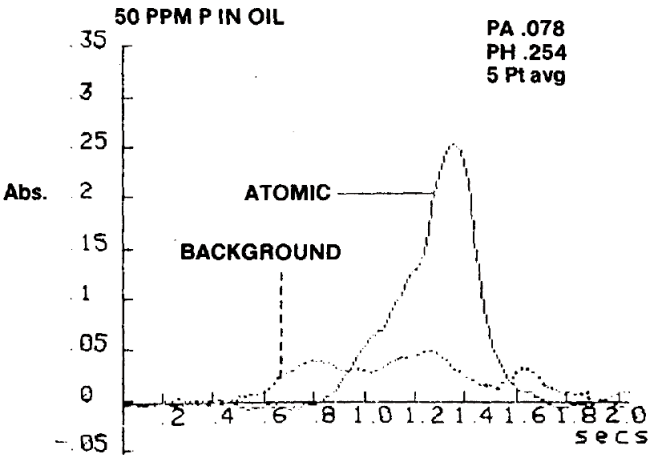

Figure 5. HP-85 Graphics printout CRA-90 Carbon rod atomizer.

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