



Direct Determination of Phosphorus in Aqueous Matrices by Atomic Absorption

Application Note

Atomic Absorption

Author

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Introduction

The determination of phosphorus is important in the quality control of many products and in some environmental studies. Phosphorus determinations can be very tedious and time consuming depending on the procedure used. Because of the increasing interest in phosphorus, many analysts have turned to Atomic Absorption. It is comparatively quick and has few interferences. Analysts have found that phosphorus is less sensitive than other elements normally determined by flame AA. The most sensitive phosphorus resonance lines are in the vacuum ultraviolet region. Thus, a less sensitive non-resonance line must be used [1]. Normal phosphorus concentrations for flame analysis range from 400 to 8000 $\mu\text{g/mL}$.

Sample Preparation

For substances that dissolve readily in water, no digestion procedure is necessary. Two problems encountered in the direct determination of phosphorus by AA are the high dissolved solids solutions and normal working range of phosphorus. The level of dissolved solids should not exceed 7%. This can be a problem if the concentration of phosphorus to be determined is low. In some cases, it is better to use the carbon rod atomizer rather than trying to concentrate the phosphorus. An additional problem may be caused by foaming which may occur with substances similar to soaps. This needs to be minimized to ensure reproducible nebulization and drainage of the spray chamber. Foaming may be minimized by diluting the sample as much as possible.

For samples that require digestion, two procedures are available. The first is dry ashing followed by dilute acid solubilization. Because many phosphates and phosphides volatilize at approximately 200 °C, ashing of samples should only be attempted using an ash aid. Some phosphate and phosphide compounds boil or dissociate at very high temperatures (1100 °C or higher). Examples of elements forming these compounds are Ca, Co, Cr, Cu, Fe, La, Ni, Sr, Y and Zn. One of these elements could be added to samples to minimize the volatilization of phosphorus.



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Wet digestion with acids is the second procedure available. This procedure will normally eliminate loss of phosphorus by volatilization. The acids selected depend on sample type.

Results — Flame AA

The calibration curve shown in Figure 1 exemplifies the normal working range for phosphorus. This typically is from 400 to 8000 $\mu\text{g/mL}$ P. The upper concentration limit will depend on the dissolved solids content of solutions analyzed. The upper limit is 20,000 $\mu\text{g/mL}$ only if H_3PO_4 solutions are analyzed.

Soap containing the phosphorus compound $\text{Na}_5\text{P}_3\text{H}_{10}\text{6H}_2\text{O}$ is an example of high dissolved solids solutions which may be encountered. This solution had to be diluted considerably because of the high dissolved solids content and foaming. Standards were prepared with phosphoric acid. The phosphorus concentration in the soap was determined against the phosphoric acid standards and also by the method of standard additions. Results obtained were the same for both techniques. Other forms of phosphorus were also analyzed; these were KH_2PO_4 , NaH_2PO_4 , and Na_2HPO_4 . All forms gave results comparable to the soap solution and phosphoric acid standards.

Parameters used for the analysis were as follows:

AA-475 Instrument Parameters

Wavelength	213.6 nm
SBW	0.2 nm
Electrodeless Discharge Lamp (EDL)	
EDL power	6 watts
AA lamp current	5 mA (7 mA on the AA-875)
Flame	Nitrous oxide-acetylene

Note: Light path should be 1 cm above the burner. Reproducibility for the phosphorus determination by flame AA is also shown in Figure 1.

A two-second integration time was utilized to minimize the effect of high dissolved solids solutions which may cause plugging of the nebulizer and buildup in or on the burner head. Short integration times, aspiration of distilled water between samples and standard solutions, and an increase of oxidant flow over the minimum will ensure better reproducibility. If any build-up occurs on the burner, this should be removed (with the flame OFF) using a suitable implement.

A phosphorus hollow cathode lamp may be used in place of the EDL. The characteristic concentration (sensitivity) will be comparable but the detection limit will be poorer. This is due to increased noise levels resulting from the low light intensity of the hollow cathode lamp. Using an EDL, the characteristic concentration and detection limit for phosphorus is 125 $\mu\text{g/mL}$ and 40 $\mu\text{g/mL}$ respectively. For concentrations less than 400 $\mu\text{g/mL}$, alternative forms of analysis should be employed.

BAR GRAPH GROUP	CONC. OF P	MEAN INT. ABS	% R.S.D. INT. ABS
1	2130	046	1.25
2	4260	110	1.82
3	6400	172	1.34
4	8530	230	0.79
5	6400	173	0.33
6	4260	109	1.40
7	2130	049	3.14

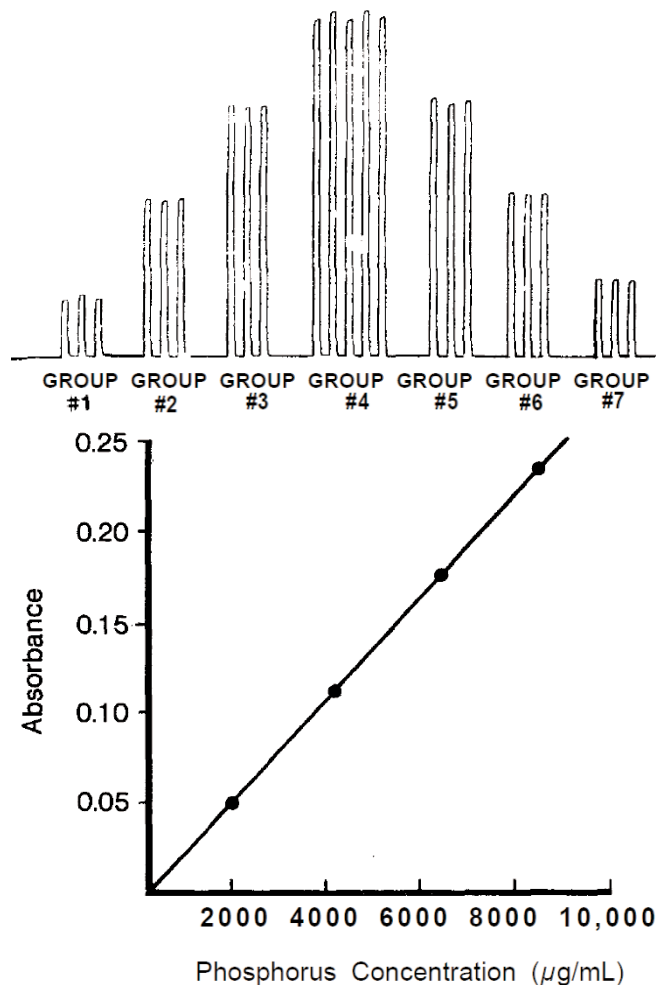


Figure 1. Flame determination of phosphorus in water.

Results — Furnace AA

Carbon rod analysis can be used for determining phosphorus concentrations which are too low to be determined by the flame. Colorimetric methods where molybdenum is complexed with ortho-phosphate are also very sensitive. Colorimetric methods work well when sample matrices are interference free and all phosphorus is in the ortho-phosphate form. The phosphorus form does not affect total phosphorus determinations by carbon rod.

Sample preparation for the carbon rod is basically the same as for flame analysis and the same precautions must be taken. More flexibility is available however. Solid samples, slurries, high dissolved solids solutions, and high acid solutions can be analyzed directly on the carbon rod. However, discussion will be limited to samples in solution.

Because many forms of phosphorus volatilize at about 200 °C a stabilizer must be added to the samples. 0.2% lanthanum nitrate has been suggested [1]. Lanthanum causes rapid degradation of graphite parts. It also has a very high boiling point (3469 °C) resulting in a build-up of lanthanum in the sample tube which eventually causes a loss in sensitivity. Lastly, lanthanum is expensive. In order to find an element more suitable for stabilization, the following elements were studied: Ca, Co, Cr, Cu, Fe, Ni and Zn. Nickel was the only element which gave improved sensitivity and longer tube life.

A study was carried out to determine the optimum nickel concentration for stabilization. Figure 2 shows the results obtained. Although 5000 µg/mL of Ni gives the best sensitivity, reproducibility and life of the graphite tubes is poor. 1000 µg/mL Ni gave the best overall performance with respect to sensitivity, reproducibility and tube life. Figure 3 shows sensitivity and reproducibility using 1000 µg/mL Ni for stabilization. Replicate readings using 10 µL injections of 100 µg/mL P gave a mean absorbance of 0.409. The relative standard deviation was 3.93%. Precision will normally range from 2.5 to 6.5% (RSD).

Parameters used for the analysis were as follows:

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

Dry	100 °C for 45 seconds
Maximum ash	1400 °C
Recommended ash	1100 °C for 15 seconds
Atomize	2500 °C (hold ¼ seconds)
Ramp	600 °C/sec
Sheath gas	Argon

Note: Nitrogen may be used with a slight loss in sensitivity. Stabilizer: 0.1% Ni (as nickel nitrate).

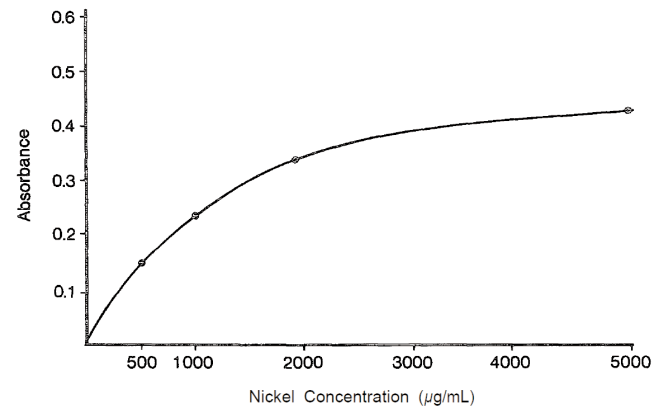


Figure 2. Absorbance from 50 µg/mL phosphorus in water at various nickel concentrations. CRA-90 Carbon rod atomizer.

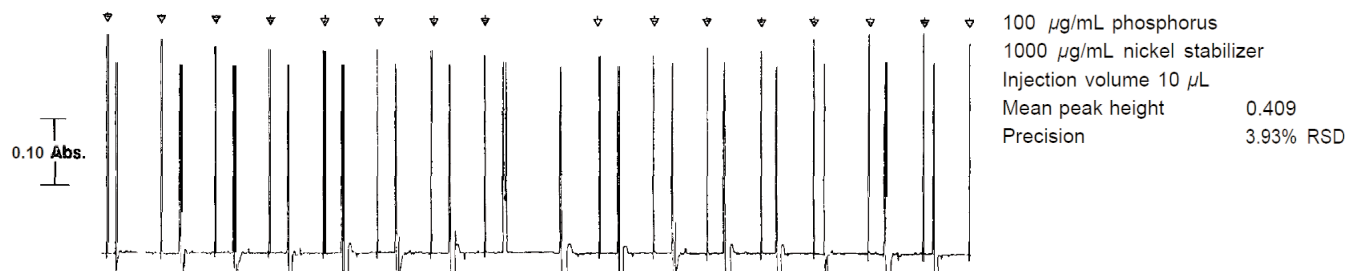


Figure 3. Reproducibility for phosphorus in water. CRA-90 Carbon rod atomizer.

Figure 4 shows a calibration curve for phosphorus determinations using the CRA-90. The normal working range is 1 — 200 µg/mL P. If the concentration of phosphorus exceeds 200 µg/mL, larger concentrations of the nickel stabilizer must be used. If phosphorus concentrations are less than 50 µg/mL, the nickel stabilizer level should be reduced by half. For routine determinations, the nickel stabilizer should be at the 1000 µg/mL level in the blank, standards, and samples. The characteristic concentration (sensitivity) for this determination is 1.5 ng P absolute.

Figure 5 is a graphics printout from the HP-85 computer for AA. Peak height, peak area, background absorbance, and atomic absorbance are shown. The CRA is at the Programmed Atomize temperature in 2.3 seconds. Several conclusions can be made using the graphics. The atomic peak is completed before the Programmed Atomize temperature is obtained. The phosphorus peak appears at approximately 1580 °C and attains its maximum absorbance at approximately 1880 °C. Therefore, if large quantities of nickel were not present, a lower atomization temperature could be used. The high atomize temperature is necessary to drive off the large concentrations of nickel, thus keeping conditions in the tube uniform. Figure 5 also shows that some background is present. Therefore, background correction should be used. The use of computer graphics can simplify method development.

CONC OF P	MEAN PEAK HEIGHT	% RSD PEAK HEIGHT	MEAN PEAK AREA	% RSD PEAK AREA
5.0	063	9.7	027	2.6
10.0	112	11.0	045	12.0
20.0	194	4.7	065	11.9
50.0	246	3.5	118	8.7

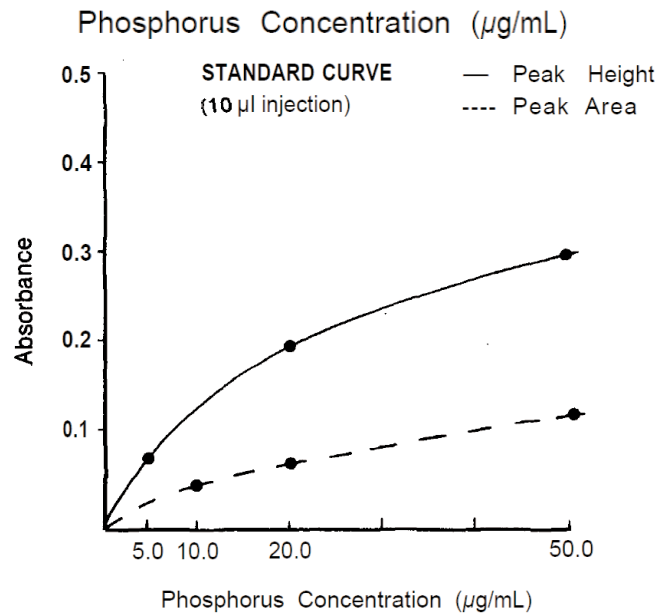
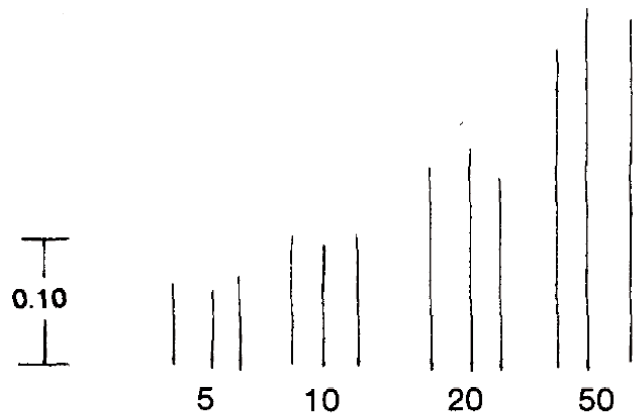


Figure 4. CRA-90 determination of phosphorus in water.

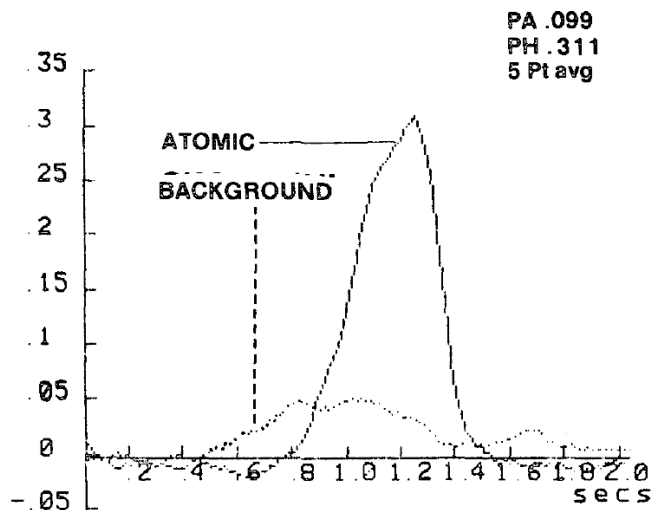


Figure 5. HP 85 graphics printout. CRA-90 carbon rod atomizer.

Conclusion

The direct determination of phosphorus by AA is simple and straightforward. Sample preparation can be kept to a minimum. The normal working range is 400–8000 $\mu\text{g/mL}$ P for flame determinations. For lower concentrations, the carbon rod should be used. When using the carbon rod, a stabilizer (1000 $\mu\text{g/mL}$ Ni) must be added to all solutions. The normal working range is 4–200 $\mu\text{g/mL}$ P for carbon rod determinations. For the analyst faced with the task of determining phosphorus in aqueous matrices, atomic absorption provides a quick, reliable means of analysis.

References

- 1 M. W. Routh, "Direct Determination of Phosphorus by Atomic Absorption", Varian Instruments at Work, Number AA-1, August 1979.
- 2 CRC Handbook of Chemistry and Physics.

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