

application note

Cintra 10e—Enhanced Sensitivity from 600–1,200 nm, Analysis of Phosphorus to Sub-ppb Levels

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Introduction

The analysis of phosphorus is of importance in environmental and industrial type monitoring applications. Phosphorus has been traditionally measured in solutions using a UV-Visible Spectrometer at the compromised 470 nm or the 690 nm wavelengths¹. These methods have poor detection limits and suffer from the phosphorous-complex formation taking a relatively long time to stabilize as well as producing unstable complexes.

The most sensitive 830 nm wavelength has not been commonly utilized due to very low light throughput of conventional spectrometers at this wavelength.

The reason for this is that spectrometers, that utilise a photo multiplier detector usually have an upper wavelength range of 900 nm. These instruments have very poor light throughput in the 600 to 900 nm range and hence cannot utilise the most sensitive 830 nm wavelength.

The Cintra 10e uses a Silicon Photodiode and advanced optics design, which enables a wavelength range up to 1,200 nm. The Cintra 10e also has significantly increased light throughput in the important 830 nm wavelength range.

The Molybdenum Blue phosphorous method² is a very sensitive method for the determination of phosphorus. When

this method is used in conjunction with a spectrometer with ample light throughput at 830 nm, such as the Cintra 10e, then phosphorus analyses can be determined at sub ppb concentrations. The Molybdenum Blue phosphorous method is not only easier to use than conventional methods but the blue phosphorous-molybdenum complex formed is produced very quickly and is stable for over 24 hours. This enables quick turn around time for sample analysis because long stabilization times required for complex formation (as occurs in conventional methods), are not required. As the blue phosphorous-molybdenum complex is very stable, samples do not have to be analysed quickly, so large sample batches may be analysed. Conventional methods produce unstable complexes, necessitating fast analysis of small sample batches.

Equipment

Cintra 10e.
Spectral Quantify Application.
1 cm quartz cell.

For the automated analysis of up to 270 samples, use the SDS-270 auto-sampler and the auto-sipper with flow through cell.

Cintra 10e enhanced energy above 630 nm

A Raw Light Scan is the best way to visually determine the light throughput to the detector at various wavelengths. The photomultiplier gain is kept constant and light scanned across the wavelength range. Figure 1 graphically illustrates the superiority of the Cintra 10e over conventional spectrometers in regards to light throughput above 630 nm. The Cintra 10e has a flat energy response from 630 to 760 nm, then it peaks at 770 nm drops in intensity at 800 nm and then peaks again at 1,000 nm. The energy response for a conventional spectrometer is already low at 600 nm and drops exponentially up to 900 nm.

At 830 nm the energy response of the Cintra 10e is 18.4%. Compare this to a conventional spectrometer which has an energy response at 830 nm of 0.4%. The energy response at 830 nm is nearly 50 times higher in the Cintra 10e compared to a conventional spectrometer. This increase in energy at 830 nm will result in decreased photo multiplier voltage required to amplify the signal and a

subsequent decrease in noise. The decrease in noise will also lead to improved detection limits in the case of phosphorus determination.

The increased energy at 830 nm coupled with an inherently sensitive phosphorus method enables in the measurement of sub ppb phosphorus concentrations.

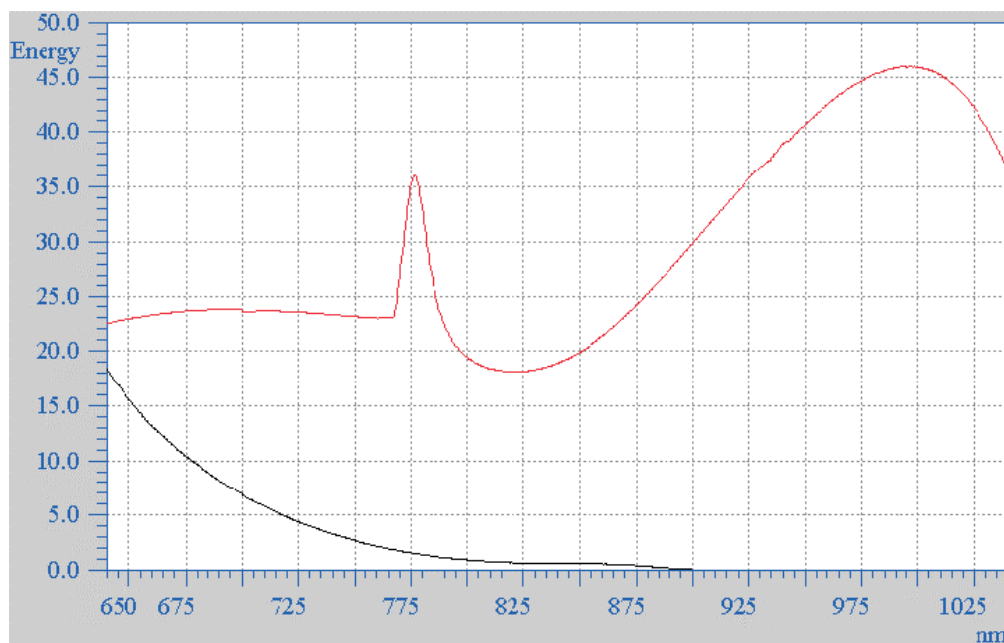


Figure 1: Comparison of the Cintra 10e raw light scan with a conventional spectrometer raw light scan

Molybdenum Blue Method

Orthophosphate and molybdate ions condense in acidic solution to form molybdophosphoric acid (phosphomolybdic acid). Upon selective reduction, (e.g., with hydrazinium sulphate) a blue colour is produced due to Molybdenum Blue of uncertain composition. The intensity of the blue colour is proportional to the amount of phosphate initially incorporated into the heteropoly acid. If the acidity at the time of reduction is 0.5 M in sulphuric acid and hydrazinium sulphate is the reductant then the resulting blue complex exhibits a maximum absorbance at 820–830 nm.

Ions which form heteropoly acids, such as silicate, arsenate, germanate and tungstate should be absent. Silicate may be removed by fuming with perchloric acid to dehydrate the silicic acid and render it insoluble. Arsenate may be volatilized as arsenic (III) bromide from a hydrobromic-acid sulphuric acid solution. Tin and germanium are also volatilized simultaneously.

Reagents

1. *Molybdate solution.*

12.5 g of Analytical Reagent sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) was dissolved in 5 M sulphuric acid and diluted to 500 mL with 5 M sulphuric acid.

This solution is to be prepared fresh monthly.

2. *Hydrazinium sulphate solution.*

1.5 g of Analytical Reagent hydrazinium sulphate was dissolved in deionised water and diluted to 1000 mL.

This solution is to be prepared fresh monthly.

3. *Standard Phosphate solution (10 ppm P)*

0.04393 g of Analytical Reagent Potassium Dihydrogen Phosphate was dissolved in deionised water and diluted to 1000 mL. 1 mL of solution = 0.01 mg P.

This solution is to be prepared fresh weekly.

4. *Calibration Standards*

The calibration standards were prepared as per table 1. These are to be prepared fresh daily.

Volume of 10 ppm P	Final Volume	Concentration P (ppb)
0.000	50	0
0.125	50	25
0.250	50	50
0.500	50	100
1.000	50	200

Table 1: Dilution scheme for calibration standard preparation

Procedure

The sample solution should not contain more than 400 ppb of phosphorus present as the orthophosphate and should be neutral. Solutions, which have greater than 400 ppb phosphorus should be diluted or alternatively higher concentration standards can be prepared and used.

Transfer 25 mL of the solution to a 50 mL volumetric flask. Add 5.0 mL of the molybdate solution, followed by 2.0 mL of the hydrazinium sulphate solution. Make to volume with distilled/deionised water and mix well. Immerse the stoppered flasks in boiling water for 10 minutes. Remove the flasks and cool rapidly.

Shake the flasks and measure the absorbance at 830 nm against a reagent blank.

Note that the sample heating for 10 minutes ensures that the reaction has gone to completion. Studies undertaken showed that the blue colour of the phosphorus-molybdenum complex formation was complete after the 10 minute heating and no further reaction occurred. As a stable reading is obtainable immediately after the cooling step, samples can be analysed immediately unlike conventional methods such as the Vanadomolybdophosphoric acid method at 470 nm, which has a long stabilization time.

Laboratory productivity is significantly enhanced using the Molybdenum Blue method.

The blue phosphorous-molybdenum complex was found to be stable after 24 hours. This gives the analyst the flexibility that;

1. Samples do not have to be analysed immediately after they are prepared
2. Sample integrity is maintained if large batches of samples are prepared and then analysed.

immediately after preparation, large sample batches cannot be to be analysed.

Results

Table 2 lists the standard results obtained. Figure 2 graphically illustrates this data.

Even at the low phosphorus concentrations, a linear correlation was obtained between concentration and absorbance.

Concentration P (ppb)	Absorbance
0.0	0.0000
25	0.0253
50	0.0513
100	0.1042
200	0.2071

Table 2: Calibration results obtained.

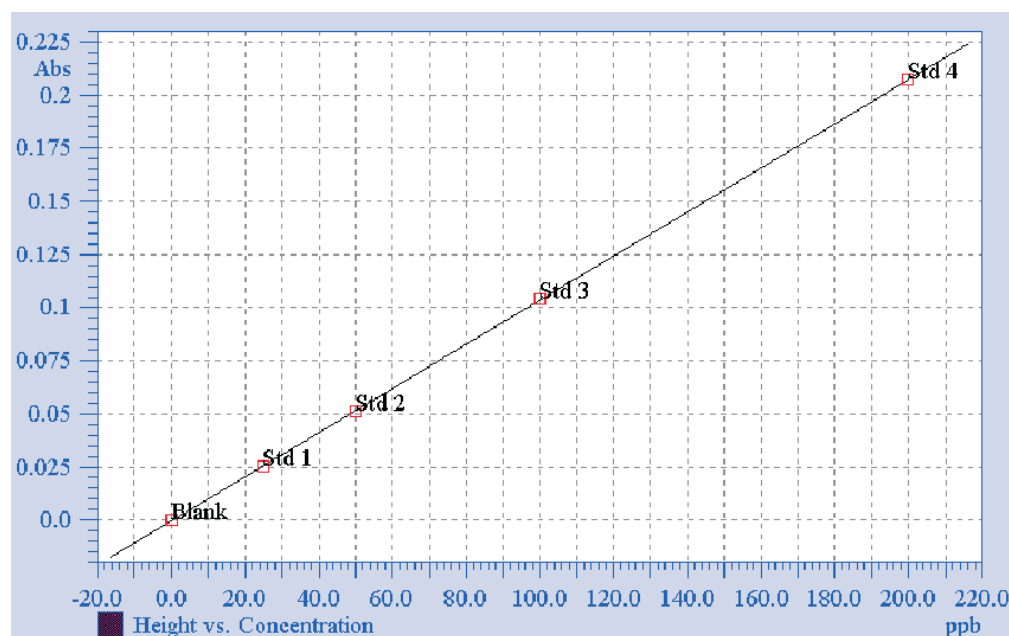


Figure 2: Calibration graph of standards from 25 to 200 ppb Phosphorus.

In contrast, conventional methods such as the Vanadomolybdophosphoric acid method at 470 nm do not form stable coloured complexes. Hence with these methods, as samples must be analysed

The detection limit was calculated by analysing a 25 ppb standard and reagent blank 10 times. Using a 3σ confidence limit, a detection limit of 0.2 ppb was obtained. This is 1000 times more

sensitive than the conventional Vanadomolybdophosphoric acid method at 470 nm, which has a detection limit of 200 ppb.

Detection limit (ppb) comparison of two methods	
Molybdenum Blue at 830 nm	0.2 ppb
Vanadomolybdophosphoric acid at 470 nm	200 ppb

Table 3: Comparison of detection limits (ppb).

Conclusion

The Cintra 10e together with the Molybdenum Blue Method offers analysts a thousand-fold improvement in detection limit over conventional phosphorus methods.

The Molybdenum Blue method offers the analyst the capability of analysing very low levels of phosphorus in water samples with confidence. The Molybdenum Blue complex forms very quickly and is very stable for a long time period thus ensuring that sample analysis can be performed quickly and that sample integrity is maintained for large batch sizes.

References

1. *Standard Methods for the Examination of Water and Wastewater*, APHA, AWWA, WPCF; USA 1985, 16th Edition.
2. *Vogel's Textbook of Quantitative Inorganic Analysis, Vogel Handbook of Inorganic Chemistry*, J. Bassett, R.C. Denney, G.H. Jeffery and J. Mendham, UK, 1979, 4th Edition.

