

Adaptation of the Spectrophotometer to the Analysis of Water

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General Procedures for Flame Spectrophotometer Analyses

The Beckman model DU quartz spectrophotometer is set to measure the intensity of one of the characteristic wavelengths of light produced by exciting the elements in question in an oxygen-natural gas flame.

When all other conditions are kept constant the light intensity of each specific wavelength is proportionate to the rate of introduction of the element into the flame. The rate at which a solution of the element is introduced is kept constant by forcing it to pass through a capillary tube under a constant pressure differential by means of an air aspirator. The light intensity must then be proportionate to the concentration of the element in the solution. Previous calibration of the capillary tube using standard solutions of varying concentrations makes it possible to relate the light intensities of these known standards to the light emitted from like elements in the water under examination.

Certain few ions are of such a character that they affect somewhat the light intensity emitted by certain elements. The following procedures are designated to overcome such interferences. All waters must be first filtered. This conforms to the Association of Official Agricultural Chemists' procedure and is necessary to prevent plugging of the atomizer tip. One hundred ml. of filtered water will be more than adequate for the eight constituents listed below. Avoid dust and lint particles from towelling in the solution to be tested.

The following instrument settings are constant for all flame analyses: sensitivity $2^{1/2}$ turns from full clockwise, gas 4 cm. before turning on oxygen, air 25 psi and decimal selector switch 0.1.

Determination of Sodium and Calcium

Standard Curves. Prepare two standard solutions: one containing 2,000 ppm. Na as NaCl, the other containing 2,000 ppm. Ca as CaCO₃ dissolved with HNO₃. By diluting the Na standard prepare a series of 9 solutions ranging from 0-200 ppm. Na at intervals of 25 ppm. To each of these solutions add MgCl₂ for 20 ppm. Mg, KCl for 15 ppm. K, and 100 ppm. Ca.

By diluting the Ca standard prepare 4 series of 9 solutions each ranging from 0-200 ppm. Ca at intervals of 25 ppm. To the first series add no Na, second series add 50 ppm. Na, third series add 100 ppm. Na, and fourth series add 200 ppm. Na. Add Mg and K for 15 ppm. of each in all 36 solutions. The purpose of using 36 standards for the Ca calibration is to determine the extent of the distortion of the Ca determinations due to the presence of sodium. Read all the standards at the appropriate instrument setting (given below) and obtain the points for 5 calibration curves—4 for Ca and 1 for Na.

In the preliminary investigation, we produced 9 calcium curves, each with different amounts of Na, and 9 Na curves, each with different amounts of Ca. Since the effect of calcium on sodium is negligible, only one sodium curve is necessary. Although sodium appreciably affects the Ca calibration, instead of using 9 curves we found that 4 curves were adequate, these four

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being the Ca standards containing 0, 50, 100, 200 ppm. Na. Of the common anions, bicarbonate alone, at the concentrations greater than 100-200 ppm. depresses Ca emission. If necessary to decrease the bicarbonate concentration add acid and boil the sample.

Analytical Procedure. For sodium the instrument settings are as follows: Wavelength 590 mu, red phototube in place, no filter, oxygen 42 inches of water, and slit width 0.07 mm. Introduce a standard containing 200 ppm. Na only and balance the instrument at 100 transmission units. Then read the percent transmission of a solution containing 100 ppm. Na only. This reading serves as a control, which should be repeated often while analyzing samples and should not vary more than ± 0.3 transmission units during the analyses to assure that conditions have remained constant. Rinse and fill a 5-ml. Beckman beaker with the original filtered water, place under the atomizer tip and record the resulting transmission units. Dilute if necessary to bring the readings within the range of calibration.

The settings for Ca are: Wavelength 556 mu, blue phototube in place, didymium filter in place, oxygen 32 inches of water and slit width 0.30 mm. Follow the Na procedure except to substitute a solution of 200 ppm. Ca only for setting the transmission at 100. Read a solution of 100 ppm. Ca only for the curve control. The allowable tolerance is again ± 0.3 transmission units. Replace the beaker- containing the unknown under the atomizer tip and determine the transmission units. Having the resulting transmission units at both appropriate wavelengths, find the ppm. sodium then ppm. calcium from the proper calibration curve, taking into account the presence of sodium when using the calcium curves.

Determination of Potassium

Standard Curve. Prepare a standard KCl solution containing 400 ppm. K. By diluting this primary standard prepare a series of six standard solutions ranging from 0 to 100 ppm. K at intervals of 20 ppm. Each standard should contain also 50 ppm. Mg, 100 ppm. Na, and 100 ppm. Ca. The points on the curve are determined by reading the above standards at the proper instrument settings (given below). It was found that varying the concentrations of the other constituents had negligible effect on the potassium reading.

Analytical Procedure. The instrument settings: Wavelength 768 mu, red phototube in place, no filter, sensitivity $2^{7/2}$ turns from full clockwise, gas 4 cm. before turning on oxygen, 36 inches of water, air 255 psi, slit width 0.050 mm. Introduce a standard containing 100 ppm. K only and set the instrument at 100 transmission units. Then, for a control, read the percent transmission of a solution containing 40 ppm. K only. This curve control reading should not vary more than ± 0.3 transmission units during an analysis. Introduce some of the same 5 ml. portion that was used for Na and Ca. Note the transmission units and obtain the ppm. K from the standard curve. Again retain the solution for later use.

Determination of Magnesium

Standard curve. Prepare a standard solution containing 500 ppm. Mg as, $MgCl_2$. By diluting this primary standard prepare a series of 5 standard solutions ranging from 0 to 100 ppm. Mg at intervals of 25 ppm. Each standard should contain also 40 ppm. K, 100 ppm. Ca, and 100 ppm. Na. The points on the curve are determined by reading the above standards at

the proper instrument settings (given below). It was found that the varying of the concentrations of the other constituents had a negligible effect on the magnesium determination.

Analytical Procedure. The instrument settings: Wavelength 383 mu, blue phototube in place, no filter, sensitivity $2^{1/2}$ turns from full clockwise, gas 4 cm. before turning on oxygen, oxygen 56 inches of water, air 25 psi, slit 0.70 mm. Introduce a standard containing 100 ppm. Mg only and balance the instrument at 100 transmission units. Then, for a control, read the percent transmission of a solution containing 50 ppm. Mg only. This curve control reading should not vary more than + 0.1 transmission units during an analysis. Introduce a portion of the same sample that was used for Na, Ca and K. From the transmission units found, determine the corresponding ppm. Mg from the calibration curve.

Determination of Sulphates

Standard Curves. Prepare a standard solution containing 1,000 ppm. SO_4 as K_2SO_4 (I). Also prepare two standard solutions of barium—one containing 500 ppm. SO_4 equivalent as $\text{Ba}(\text{NO}_3)_2$ plus 1 gram sodium acetate per liter (II); the other containing 250 ppm. SO_4 equivalent as $\text{Ba}(\text{NO}_3)_2$ plus 0.5 gram sodium acetate per liter (III).

Two calibration curves are advantageous, one curve for 200 to 500 ppm. SO_4 , the other for 0 to 200 ppm. SO_4 . By diluting (I), prepare a series of secondary standards ranging from 200 to 500 SO_4 at intervals of 50 ppm. To ten ml. of each of these sulphate standards add 10 ml. of (II). Warm in a stoppered flask. Cool and filter a portion into a 5-ml. beaker. There are then seven solutions containing $\text{Ba}(\text{NO}_3)_2$, ranging from 150 to 0 ppm. SO_4 equivalent. The excess Ba is read on the flame photometer. By diluting (I) prepare another series of secondary standards ranging from 0-200 ppm. SO_4 at 25-ppm. intervals. To 10 ml. of each of these solutions add 10 ml. of (III), warm in a small stoppered flask and treat similarly to above. The concentrations are shown in the accompanying table:

Table 1.

For the 200-500 ppm. SO_4^* curve:									
ppm. SO_4^* in secondary standard	200	250	300	350	400	450	500		
ppm. SO_4 after 1:1 dilution	100	125	150	175	200	225	250		
ppm. SO_4 equivalent as $\text{Ba}(\text{NO}_3)_2$	250	250	250	250	250	250	250		
ppm. SO_4 equivalent in excess	150	125	100	75	50	25	0		
For the 0-200 ppm. SO_4 curve:									
ppm. SO_4 in secondary standard	0	25	50	75	100	125	150	175	200
ppm. SO_4 after 1:1 dilution	0	12.5	25.	37.5	50.	62.5	75.	87.5	100
ppm. SO_4 equivalent as $\text{Ba}(\text{NO}_3)_2$	125	125	125	125	125	125	125	125	125
ppm. SO_4 equivalent in excess	125	112.5	100.	87.5	75.	62.5	50.	37.5	25.

The instrument settings are as follows: Wavelength 831 mu, red phototube in place, no filter, sensitivity $2^{1/2}$ turns from full clockwise, gas 4 cm. before turning on oxygen, oxygen 34 inches of water, air 25 psi. For the 200 to 500 ppm. SO_4 series, adjust the slit width to 0.50 mm. and balance at 100 transmission units using the secondary SO_4 standard which originally contained 200 ppm. SO_4 . For the 0 to 200 ppm. SO_4 series, adjust the slit width to 0.52 mm. and balance at 100 transmission units using the secondary SO_4 standard which originally contained 0 ppm. SO_4 .

Analytical Procedure. If sample contains more than 500 ppm. SO_4 dilute to 200 to 500 range. Pipette 10 ml. of the sample water into a 50-ml.

flask. If sample contains 200 to 500 ppm. SO_4 , add 10 ml. of (II). If sample contains 0-200 ppm. SO_4 , add 10 ml. of (III). Stopper, warm and allow to stand, then filter. Introduce a portion of this filtrate into the flame atomizer. Record the transmission units and obtain the ppm. SO_4 from the proper calibration curve.

Procedure for Chlorides—Tentative

The method is similar to the procedure for sulphate determination. To a series of standard chloride solutions add a measured amount of standard silver nitrate which is an excess. Filter and read the excess silver on the spectrophotometer. The instrument settings are as follows: Wavelength 338.3 mu, blue phototube in place, no filter, sensitivity $2^{1/2}$ turns from full clockwise, gas 4 cm. before turning on oxygen, oxygen 56 inches of water, air 25 psi, slit width 1.0 mm. The curve should extend to 100 ppm. chloride on original sample. The detectability of silver is approximately the same as barium.

General Procedures for Absorption Spectrophotometer Analysis

Standard procedures are used to develop the colors of the ions in question. The absorption of specific wavelengths of light is measured using the spectrophotometer. It is possible to select any wide or narrow band from the entire visible or ultraviolet portion of the light spectrum. Critical selection of a narrow band of wavelengths permits analyses with a minimum of interference and high precision. Calibration curves made from standard samples expedite and simplify the analytical procedure.

All colors to be measured are produced by methods as described in *Methods of Analysis*, Association of Official Agricultural Chemists, 6th edition, 1945. All instrument settings reported here were found by experiment. Many wavelengths were tried until one was found which gave maximum differences between those standards which fall in the range of the unknown. At the same time the wavelengths chosen were such as to give reproducible results with duplicate standards.

Procedure for Nitrates

The color to be measured is produced by the reaction of nitrates with phenodisulphonic acid. The intensities of colors produced by nitrate solutions ranging from 0 to 0.10 mg. of NO_3 are used to prepare a standard curve. The intensities of color produced by unknown solution, similarly treated, are compared with the standard curve to determine the quantity of nitrate present. The intensities are measured by first placing distilled water free of turbidity in a cell in the light path of the spectrophotometer and the instrument is balanced at 100 percent transmission. The prepared colored solution is then placed in the light bath and the transmission noted. Instrument settings to be used are as follows: Wavelength 380 mu, blue phototube in place, slit width 0.055 mm. sensitivity $2^{1/2}$ turns from full clockwise, and the decimal switch at 1.0.

Procedure for Ammonia

The color to be measured is produced by the reaction of ammonia with Nessler's reagent. The intensities of colors so produced by known quantities of NH_3 are used to prepare a standard curve. The intensity of color produced by a similarly treated unknown water is compared with the standard curve to determine the quantity of NH_3 present.

The intensities are measured as under nitrates except that the instru-

ment settings are as follows: Wavelength 445 mu, blue phototube in place, slit width 0.025 mm. sensitivity $21\frac{1}{2}$ turns from full clockwise, and decimal switch at 1.0. After the colors have been developed, the samples, especially the ones of lower concentration, upon prolonged standing may darken to a degree perceptible to the spectrophotometer. For this reason the intensities should be measured just 10 minutes after addition to the Nessler's reagent. Also, a check of the standard curve should be made each time new reagents are prepared.

Analysis for Phosphates

The color to be measured is produced by the reaction of phosphate with ammonium molybdate in 10N H_2SO_4 and stannous chloride. The same general plan of analysis is used as for nitrates. Instrument settings are as follows: Wavelength 700 mu, red phototube in place, slit width .025 mm. sensitivity $2^{1/2}$ turns from full clockwise, and decimal switch at 1.0.

Accuracy and Precision

Several workers in this field, including some noted in the bibliography, have evaluated the accuracy of the spectrophotometer in absolute terms, that is, by means of standard deviations, etc. The spectrophotometer is a relatively new instrument. It is suggested that its use replace older techniques. A more practical evaluation of the instrument might then be its direct comparison against the older procedures. Such a comparison is more difficult to analyze but we felt it worthwhile.

Nine chemists, most of them with many years of experience, analyzed widely differing waters using slight modifications of the Association of Official Agricultural Chemists' methods. Of these waters, 34 were shipped to our laboratory and analyzed by means of the spectrophotometer. In the case of those elements using the flame attachment, the average deviations were: calcium, 9 ppm.; magnesium, 1 ppm.; sodium, 5 ppm.; potassium, 4 ppm.; and sulphate, 20 ppm.

Comparing the slopes of the calibration curves of the above metals, it is seen that the accuracy of the magnesium determination is about one-third of the other flame determinations. We adduce, since the poorest spectroscopic method gave the best comparative results, that the accuracy of the two were of the same order, and furthermore, that the accuracy of the spectrophotometer methods was greater in the case of calcium, sodium, potassium and sulphate. Comparison of the absorption colorimetry techniques showed an average deviation for ammonia of 5 ppm. and for nitrates 12 ppm.

Tests for both ions require considerable preparation before the colors are finally obtained. Care must be exercised to reduce errors in technique of color preparation in order to utilize fully the high precision inherent in the spectrophotometer.

Summary

Techniques are outlined for the use of the Beckman model DU spectrophotometer and its flame attachment for analyses for eight ions. In using the flame attachment very tedious standard techniques have been replaced by a few very simple operations. Time for analysis has been greatly decreased, the quantity of sample required greatly decreased, and the accuracy of analysis generally increased. The absorption colorimeter techniques described do not save a great deal of time but accuracy is improved.

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