## 23. Turbidimetry – Determination of sulphates

The blue color of the sky during the day and the red color of the sun at sunset result from the scattering of light by small particles of dust, molecules of water, and other gases in the atmosphere. The efficiency with which light is scattered depends on its wavelength. The sky is blue because violet and blue light are scattered to a greater extent than other, longer wavelengths of light.

For the same reason, the sun appears to be red when observed at sunset because red light is less efficiently scattered and, therefore, transmitted to a greater extent than other wavelengths of light. The earliest quantitative applications of scattering, which date from the early 1900s, used the elastic scattering of light to determine the concentration of colloidal particles in a suspension.

Nowadays, this method is widely applied for analysis of some ions in natural waters, but also contaminants in air (smokes, aerosols), chemical gas warfare, some bacteria, the dispersed phase in colloidal emulsions (like milk), to determine the effectiveness of filtration, to determine fats and lubricators, for many biochemical analyses (urine, blood etc.), for determination of proteins and others.

Turbidimetry is an optical method based on measuring the transmitted light (I_t) which is related to the concentration of scattering particles. A variety of this method, in which the detector is situated at a right angle in respect to the beam of the incident light is known as **nephelometry**.
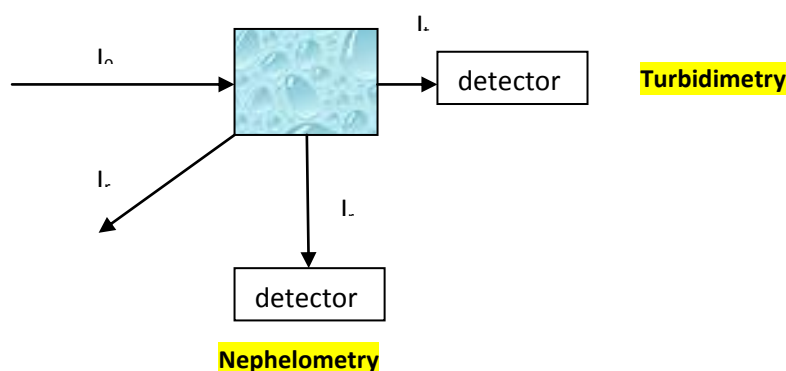
The incident light of I_0 intensity passing through the examined sample may be scattered (I_r) and/or absorbed (I_{abs}). The intensity of the radiation transmitted I_t is therefore equal to:

$$I_t = I_0 - I_{abs} - I_r$$

For true (molecular) solutions I_r is practically omitted, therefore: $I_t = I_0 - I_{abs}.$
For colorless cloudy solutions I_{abs} is omitted, then: $I_t = I_0 - I_r.$

In turbidimetry the measured quantity is absorbance A_p, also called a turbidity value S which is related to the following equation:

$$A_p = T = S = \log \frac{I_0}{I_t} = k \cdot \frac{b^3}{b^4 + a\lambda^4} \cdot c \cdot l = K \cdot c \cdot l$$

where:
I_0 – intensity of the incident light,
I_t – intensity of the transmitted light through the cloudy solution,
k, a, K – constants dependent on the type of suspension,
c – concentration,
l – thickness of the sample,
b – average value of the cross-section of the particles,
λ – wavelength of the incident light.
The proportionality constant K depends on the particle size and shape.

To make measurements reproducible it is important that the particle size is maintained constant. Therefore the following items should be considered:

1. The relative concentration of ingredients must be controlled.
2. The relative ratios of reactants must be constant.
3. The manner, order of addition and rate of mixing must be constant.
4. The nature of other solutions present must be considered and, if necessary, protective colloids added to avoid protein precipitation.
5. The temperature must be maintained constant.

A number of inorganic cations and anions can be determined by precipitating them under well-defined conditions and measuring the transmittance of radiation from the precipitated particles. The transmittance is proportional to the concentration of the scattering particles, which, in turn, is related by the stoichiometry of the precipitation reaction to the analyte's concentration. Examples of analytes that have been determined in this way are listed below:

Selected precipitates used in turbidimetric method

Analyte	Precipitant	Precipitate
Ag^+	NaCl	AgCl
Ca^{2+}	$Na_2C_2O_4$	CaC_2O_4
Cl^-	$AgNO_3$	AgCl
CN^-	$AgNO_3$	AgCN
CO_3^{2-}	$BaCl_2$	$BaCO_3$
F^-	$CaCl_2$	CaF_2
SO_4^{2-}	$BaCl_2$	$BaSO_4$
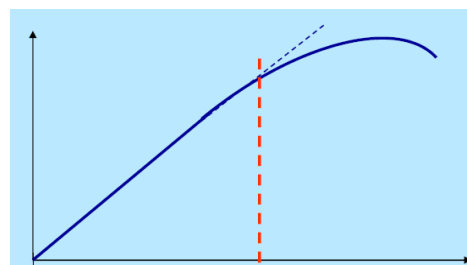
The unknown concentration of an analyte (scattering particles) is determined on the basis of a calibration curve $A_p=f(c)$, which is obtained from measurements of standard solutions.

This method is widely applied in analysis of naturally opaque systems, like sea, lake, or mineral waters, insulin, cholesterol, hemoglobin, antibiotics, in biochemical analysis of nucleic acids and enzymes, etc.

Turbidimetric determination of sulphates(VI) in natural water

For low contents of SO_4^{2-} ions in solution, barium sulphate forming after addition of $BaCl_2$ does not fall down but remains suspended in the solution, causing opacity. Precipitation is carried on in diluted HCl. Opacity develops in time and stabilizes after few minutes. Determination of sulphates is made at room temperature, increase of temperature causes "ageing" of the precipitate. Addition of alcohol decreases solubility of $BaSO_4$ and increases its dispersity, addition of glycol or glycerol stabilizes the opacity.

Chemicals and solutions
1. Stabilizing solution: 50 mL glycerol, 30 mL concentrated HCl, 300 mL distilled water, 100 mL 95% ethyl or isopropyl alcohol, 75 g NaCl (high ionic strength and acidity prevent formation of microcrystalline $BaSO_4$, glycerol and alcohol stabilize the suspension);
2. $BaCl_2$ pure for analysis, crystalline;
3. The initial solution of sulphates: ca. 0.2 mg SO_4^{2-}/mL: weigh precisely, using an analytical balance, approx. 0.3 g anhydrous Na_2SO_4 (dried at 105°C), dissolve it in H_2O and add water to the total volume 1L. Calculate the exact concentration of sulphate anion in this solution.

Determination of sulfates in water using a turbidimeter

Description of method. Adding $BaCl_2$ to an acidified sample precipitates SO_4^{2-} as $BaSO_4$. Concentration of SO_4^{2-} should be determined turbidimetrically using an incident source of radiation of 420 nm. We will apply, however, much simpler device, where white light of luminescent diode (⊗), after passing through the sample, illuminates the photoresistor (▱), which resistance is displayed by universal, popular measuring instrument (ohmmeter).

External standards containing known concentrations of SO_4^{2-} are used to standardize the method.

Procedure

Calibration curves are prepared by diluting the initial solution of sulphates: pour to ten beakers á 200-250 mL the following volumes of the initial solution: : 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 mL, this corresponds to the contents of (approx.) 0, 2, 4, 6, 8, 10, 12, 14, 16, and 18 mg SO_4^{2-}. Using the exact concentration of your stock solution prepared before, calculate the exact concentrations of the solutions of the series.

The standards and a reagent blank must be treated in exactly the same fashion as samples.

Add to each beaker 5 mL of the stabilizing solution and complete the volumes of solutions to 100 mL using distilled water. Mix the content 30 sec by the magnetic stirrer. It should operate at the same speed for all samples and standards – not too fast but vigorously.

Add 5 mL of the stabilizing solution to the unknown sample, complete its volume to 100 mL and mix during 30 sec.

A portion of crystalline $BaCl_2$ is added to all the beakers using a measuring spoon whose capacity is 0.3–0.4 mL, precipitating the SO_4^{2-} as $BaSO_4$.

Timing begins when the $BaCl_2$ is added and the solution and precipitate are allowed to stir for exactly 1 min. At the end of the stirring period a portion of the suspension is poured into the turbidimeter cell, and the resistance is measured at 15-s intervals for 1 min.

Both mean and maximum resistance recorded during this period are the analytical signals.

After the measurement, the content of the turbidimeter cell should be returned to the mother beaker.

Report

The report should contain the short description of the procedure, the data obtained for the standard solutions and for the sample, the plot of these data showing the graphical determination of SO_4^{2-} content, as well as that determined from the regression curve. Use any data sheet available, the student should decide which polynomial is the best for description of the calibration curve, and should use this polynomial after regression for numerical calculation of SO_4^{2-} content in the sample.

An example of the calibration plot and the analysis (the result is ca. 9 mg of SO_4^{2-}) is below:
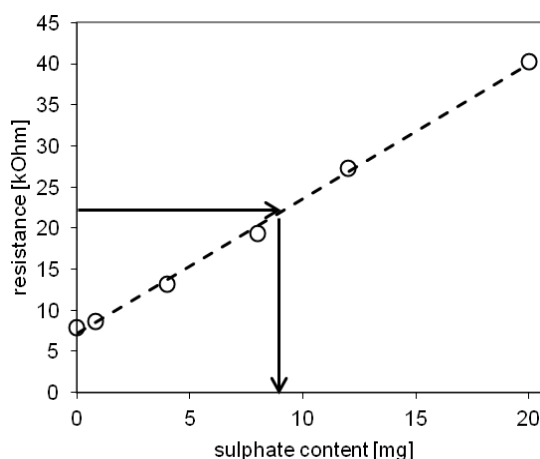
Sources:

D. Harvey, „Modern Analytical Chemistry", McGraw-Hill Com., Inc., USA, 2004.

W. Szczepaniak, „Metody instrumentalne w analizie chemicznej", Wydawnictwo Naukowe PWN, Warszawa, 2002.

Z. Marczenko, M. Balcerzak, „Spektrofotometryczne metody w analizie nieorganicznej", Wydawnictwo Naukowe PWN, Warszawa, 1998.

P.N. Palei, N.I. Udal'tsova, *Zavod. Lab.*, **30**, 151 (1964).

H.E. Hoffmann, *Z. Chem.*, **17**, 147 (1977).

http://www.kchaie.uni.opole.pl/