ACTA CHEMICA SCANDINAVICA 14 (1960) 1279—1287

Optical Phenomena in Turbidimetric Analysis Applied to Sulfate Determination in Phosphoric Acid

SVEN-ERIC DAHLGREN

Research and Development Dept., AB Förenade Superfosfatfabriker, Landskrona, Sweden

A theory for optimum measuring wavelength at turbidimetric analysis is presented. As the validity of Lambert-Beer's law is limited at short wavelengths the theory has not been satisfactorily verified when applied to barium sulfate dispersions in gelatine solution. The optical properties of such dispersions have been studied and recommendations for measurements are given. A standard deviation of 1.5 % was obtained.

For a rapid and accurate determination of the sulfate content in technical phosphoric acid by wet processes, gravimetric methods are not convenient. Gravimetric methods are time consuming and considerable errors may thereby be introduced. Coprecipitation by cations can be eliminated by an ion-exchange technique, but the fact remains that the phosphate ion is among those anions giving the heaviest coprecipitation with barium sulfate.

A titrimetric method using the sodium salt of rhodizonic acid as an external indicator is rapid and simple but not very accurate, and may in some cases completely fail. Neither is the volumetric estimation of a centrifuged barium sulfate precipitate very accurate.

The two requirements mentioned seem to be most easily obtained by physical methods, primarily by turbidimetric and nephelometric determination of a barium sulfate dispersion. Precipitation in an ethyl alcohol-dipropylene glycol solution [1,2] was considered to be too cumbersome, and a gelatine solution was preferred. A turbidimetric method using gelatine has been presented by Gassner and Friedel [3]. The preparation of the test dispersion described by G. and F. was found to have some disadvantages, which have been eliminated. Further, there was a need for further study of the optical properties of the dispersion based on present knowledge of light-scattering by small particles.

THEORY — OPTIMUM MEASURING CONDITIONS FOR TURBIDIMETRIC ANALYSIS

Light-scattering phenomena by small particles are of a most complicated nature. The light is scattered in different directions and the space distribution of light intensity and polarization is a function of particle size, particle shape, light wavelength and the refractive index of the particles relative to the surrounding medium. In addition to this, the design of the optical geometry of the measuring equipment influences the data obtained. At a turbidimetric measurement part of the scattered light radiation reaches the photoreceiver of the instrument, as it takes a finite space angle. In the following, some fundamentals have been taken from the excellent monograph by van de Hulst [4] and applied to the present problem.

Let the total energy scattered in all directions by a particle be equal to the energy of the incident wave falling on the area C_{sca}, the cross section for scattering. The efficiency factor for scattering, Q_{sca}, is defined by

$$Q_{sca} = \frac{C_{sca}}{G} \tag{1}$$

where G = geometrical cross section of the particle.

Assume a spherical particle and introduce the parameter ϱ

$$\varrho = \frac{4\,\pi\,r \cdot |m-1|}{\lambda} \tag{2}$$

where r = particle radius
m = relative refractive index, that is the ratio between the refractive index relative to vacuum of the particle, and that of the dispersing medium
λ = light wave length in the medium, that is the the ratio of light wave length in vacuum and the refractive index of the dispersing medium relative to vacuum.

The physical meaning of ϱ is the phase lag suffered by the central ray that passes through the sphere along a full diameter. For non-absorbing spheres m is a real number and for absorbing ones a complex number.

In the case light absorbing particles

$$Q_{ext} = Q_{sca} + Q_{abs} \tag{3}$$

where Q_{ext} = efficiency factor for extinction, Q_{abs} = efficiency factor for absorption.

The efficiency factors for extinction and absorption are analogous to that for scattering. Thus for non-absorbing particles the efficiency factors for scattering and extinction are equal. For the present problem absorption need not to be taken into consideration.

In Fig. 1, the efficiency factor for extinction of non-absorbing spheres is shown as a function of ϱ for different values of the relative refractive index. The wave form of the extinction curves depends on interference between light transmitted through the particles and diffracted light. The "ripple"

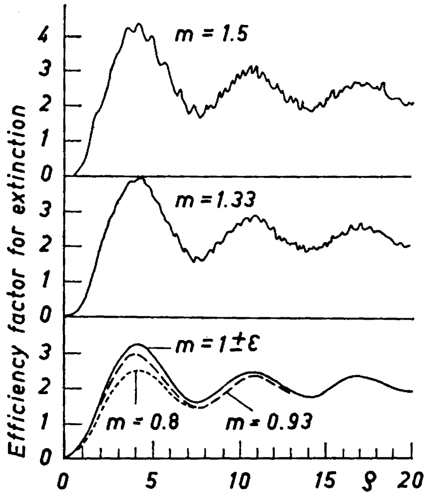

Fig. 1. Extinction curves at different relative refractive indices. After van de Hulst.

which becomes more pronounced when m increases, has no simple explanation. It is of special interest to note that the "ripple" is almost negligible for low values of m and ϱ.

In practice, dispersions of particles of uniform size are seldom found. For mixtures of particles of various sizes we define the effective radius r_{eff} as

$$r_{\text{eff}} = \frac{3}{4} \cdot \frac{\text{total particle volume}}{\text{total geometrical cross section}} \tag{4}$$

The corresponding phase lag is denoted by ϱ_{eff} and the effective efficiency factor for extinction by $\bar{Q}$. In Fig. 2 are shown extinction curves for various distributions of radii of dispersed particles when m is close to 1.

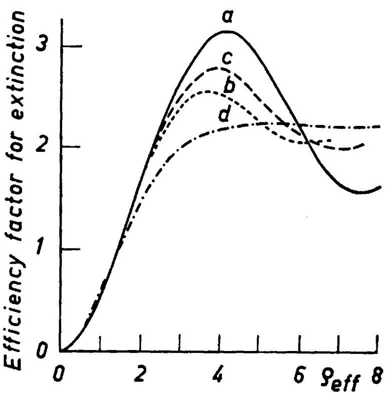

Fig. 2. Extinction curves for mixtures of particles of various sizes, all with m close to 1.

Curve a: uniform size with radius r_1
Curve b: $f(u) = u^{-1}$ for $0 < u \leqslant 1$ $r_{\mathrm{eff}} = \frac{2}{3}\, r_1$
Curve c: $f(u) = 1$ for $0 < u \leqslant 1$ $r_{\mathrm{eff}} = \frac{3}{4}\, r_1$
Curve d: $f(u) = e^{-u}$ for $0 < u < \infty$ $r_{\mathrm{eff}} = 3\, r_1$
where $u = r/r_1$ and $f(u) =$ the number distribution function.

The curves show how the typical features are washed out if particles of a range of sizes are present. Of interest is that for not too high values of ϱ_{eff} the curves nearly coincide. The transmission T of a dispersion is given by

$$T = \exp(- \overline{Q}\, \pi\, r_{\mathrm{eff}}^2 \cdot nl) \tag{5}$$

where $n =$ the number of particles per unit volume of dispersion with size reduced to r_{eff}
$l =$ the path length

On indexing the reference sample with "o" and the test sample with "t" the following expression of the extinction E is obtained

$$E = \log \frac{T_{\mathrm{o}}}{T_{\mathrm{t}}} = \frac{\overline{Q}\, \pi\, r_{\mathrm{eff}}^2 \cdot l}{\ln\, 10}\, (n_{\mathrm{t}} - n_{\mathrm{o}}) \tag{6}$$

Assume $n_{\mathrm{o}} = 0$, the concentration of the disperged material to be c, and its solubility in the dispersing medium to be s. Thus eqn. 6 changes into

$$E = \frac{k\, \overline{Q}\, l}{r_{\mathrm{eff}}}\, (c - s) \tag{7}$$

where $k =$ a proportionality constant.

Eqn. 7 holds within the region of Lambert-Beer's law. From this equation it is clear that for analytical applications, such a wave length should be chosen that a variation of the effective radius in the preparation is almost completely eliminated by a corresponding change in the effective efficiency factor for extinction. The most favourable wave length can indirectly be obtained from Fig. 2 by determining the tangent point between a straight line through the origin and the extinction curve before the first maximum. Depending on the size distribution, there are different extinction curves and a more or less flat optimum. If the measured extinction of a polydisperse dispersion is plotted against the reciprocal wave length, the curve obtained is equiform to the effective efficiency factor for extinction against ϱ_{eff}. The origin in this case is the point of infinite long wave length. From experimental data the most favourable wave length is thus directly obtained.

A consequence of the above is that the dispersion, if possible, should be prepared under such conditions that in addition to good reproducibility an effective radius is obtained, corresponding to a most favourable wave length within the measuring region of the available equipment.

It is often pointed out that the main drawback of turbidimetric methods of analysis is a lack of reproducibility in preparation of the dispersion. The presented theory shows that the effect of moderate variations in the size distribution can be eliminated. Great care in the preparation work must, however, be maintained.

Investigations by Lewis and Lothian[5] on barium sulfate dispersion with particle radius 4.6 μ gave a refractive index of 1.52 compared with 1.64 on crystalline barium sulfate. This indicates a water content of 60 % by volume of the particles, which is in accordance with specific gravity determination by sedimentation. This is explained by formation of particles through condensation of sub-microscopic units. In a medium with an refractive index close to that of water the relative refractive index will be 1.14. Since this is close to 1 the ripple on the extinction curve may be neglected for not too high values of ϱ.

EXPERIMENTAL

Solutions

Sulfate-free water. The regular distilled water was found to give a weak opalescence on addition of barium chloride. Therefore deionized distilled water has been used. Deionizing was made by Crystalab Deeminizer Model CL-5.

Gelatine solution. For preparing the gelatine solution, sulfate-free gelatine quality 1/241 Special from Deutsche Gelatinfabriken, Göttingen-Würtenberg, is used. Per liter of solution 5 g gelatine and 0.5 g thymol as a preservative are taken. After swelling for 15—30 min in deionized distilled water the mixture is heated under agitation until all gelatine has dissolved and the solution becomes clear. It is then cooled to room temperature. After a day, an increase in viscosity and weak opalescence are apparent. This depends on a transition from sol to gel state, the latter being the stable state at room temperature. On heating to 40—45°C for a few minutes and cooling to room temperature the solution again becomes clear and light-fluid. This should be repeated every day before usage. There is no apparent change in the sol state for several hours after heating. The solution may be used for at least 2 weeks.

Barium chloride — gelatine solution. Except for about 10 ml fill a 1-litre volumetric flask with above described gelatine solution. Add 20 g $BaCl_2 \cdot 2\ H_2O$ and dissolve it completely. The flask is then filled to the mark with gelatine solution.

Standard solution. 0.2718 g K_2SO_4 A R ad 500 ml with deionized distilled water. 1 ml equivalent to 0.1 mg S.

Alternatively: 0.2721 g K_2SO_4 A R ad 500 ml. 1 ml equivalent to 0.3 mg SO_4.

Alternatively: 0.2665 g K_2SO_4 A R ad 500 ml. 1 ml equivalent to 0.3 mg H_2SO_4.

Phosphoric acid solution. 200 g conc. phosphoric acid ad 1 000 ml with deionized distilled water.

Preparation of barium sulfate dispersion with known sulfate content. For work with dispersions with up to 0.35 mg S per 50 ml the standard solution is diluted with deionized distilled water 1:10. From a burette, different amounts of the diluted solution are charged into a series of dry 100 ml Erlenmeyer-flasks. The amount is preferably a multiple of 2.5 or 5 ml, but not greater than 35 ml. To each flask is added 5.0 ml of phosphoric acid solution and deionized distilled water to bring the total volume to 40.0 ml. Then 5.0 ml of gelatine solution is pipetted, and finally 5.0 ml of barium chloride-gelatine solution added drop-wise from a burette under shaking to each flask. After 10 min, extinction measurements can be carried out.

The pH of the solution should be 1—2.5, found by Gassner and Friedel[3] to be optimum.

If some other maximum sulfate content is to be investigated the dilution of the standard solution should be appropriately changed so that no more than 35 ml of the diluted solution need to be taken.

Preparation of the reference sample. In a dry 100 ml Erlenmeyer-flask 35.0 ml of deionized distilled water, 5.0 ml of phosphoric acid solution, 5.0 ml of gelatine solution and 5.0 ml of barium chloride-gelatine solution are taken and the mixture shaken.

Measuring equipment

All measurements in glass cells were made with a Beckman B spectrophotometer and all measurements in quartz cells were made with a Beckman DU spectrophotometer.

RESULTS

Behaviour at very low sulfate concentrations. When measuring at successively decreasing sulfate concentrations, a linear relationship was obtained between extinction and concentration down to a limit where a discontinuous change took place and the extinction was zero (Fig. 3). The reason is that a certain critical supersaturation, a threshold value, must be surpassed to initiate nucleation. From the figure it is clear that there is lower limit for turbidimetric determination in gelatine solution at about 0.05 mg S per 50 ml of final solution, that is about 1 ppm.

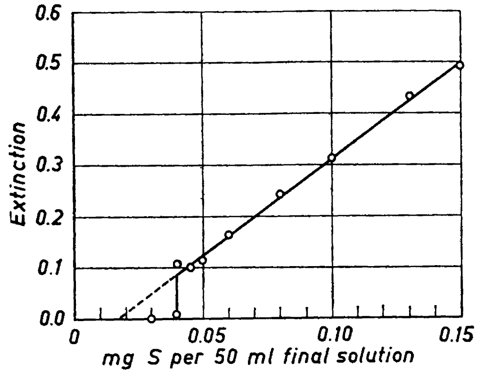

Fig. 3. Behaviour at very low sulfate concentrations. Wave length 420 mμ and 50 mm glass cells.

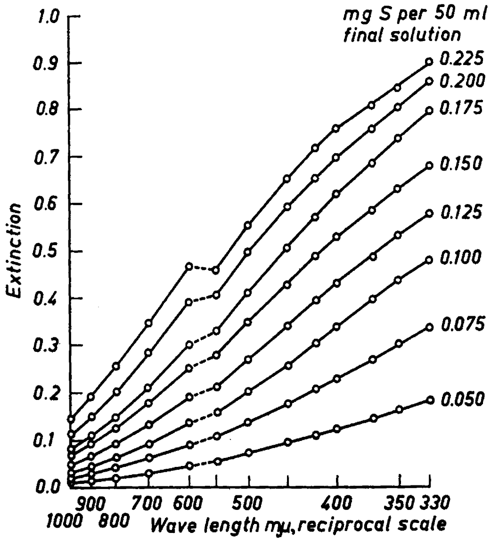

Fig. 4. Influence of light wave length on the extinction at different sulfate concentrations. 50 mm glass cells.

In an ethyl alcohol-dipropylene glycol solution the solubility of barium sulfate is completly different. It is possible in such a solution to determine nephelometrically sulfate concentrations down to 0.01 ppm.[2]

Extinction measurements in glass cells at varying sulfate concentration and light wave length. In a first series of measurements the extinction was determined over the whole wave length range of Backman B for sulfate concentrations from 0.050 to 0.225 mg S per 50 ml final solution at 0.025 intervals in 50 mm glass cells. In Fig. 4 the results are plotted with the sulfate concentration as parameter. When changing over from blue sensitive to red sensitive phototube a kink was obtained on the extinction curves, which was not the case with colorimetric determinations. Since the measurement of scattered light is sensitive to geometrical variations of the optical system in quite another degree than that of directed light, a geometrical dissimilarity between the two tubes may be responsible for the phenomenon. Since there is a reciprocal wave length scale in Fig. 4 a direct comparison with Fig. 1 is possible. This shows that the investigated range must be prior to the first maximum. At still shorter wave lengths an extinction maximum is to be expected.

In Fig. 5 the results are plotted with the wave length as parameter. The curves for 330 and 350 mμ are clearly bent and the points not so well positioned along the curve as for the other wave lengths. At 400 mμ there is a linearity up to 0.15 mg S per 50 ml which is further extended at 420 and 450 mμ. A weak tendency for the 500 and 550 mμ curves to bend in the opposite direction from the other curves is observed.

A similar series of measurements was carried out with 20 mm glass cells within the concentration range 0.05 to 0.30 mg S per 50 ml final solution at 0.05 intervals. The extinction scale in Fig. 6 is enlarged 2.5 times relative to that in Fig. 5 in order to compensate for the difference in light path of the cells. If Lambert-Beer's law is valid, the curves in the two figures should

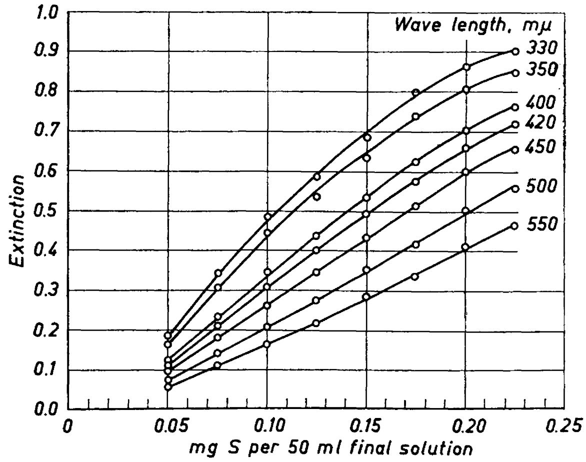

Fig. 5. Influence of sulfate concentration on the extinction at different light wave lengths using 50 mm glass cells.

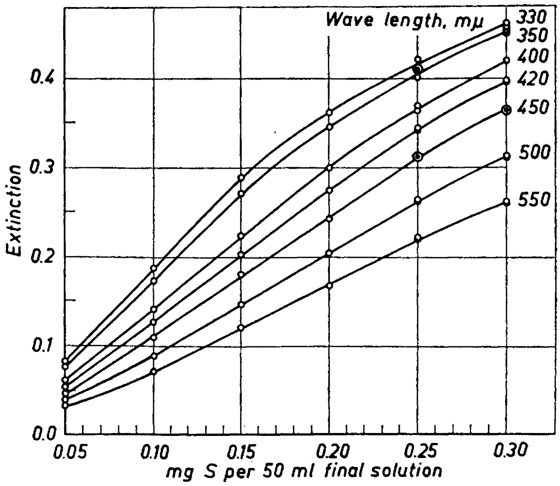

Fig. 6. Influence of sulfate concentration on the extinction at different light wave lengths using 20 mm glass cells.

coincide. After a minute parallel shift it is found that the curves for 330 and 350 mμ do not coincide, but intersect at two points. At 400 mμ they coincide up to 0.15 mg, at 420 mμ up to 0.175 mg, at 450 mμ up to 0.20 mg and at 500 and 550 mμ within the whole range.

The validity limit of Lambert-Beer's law thus varies with the wave length. A series of 11 solutions containing 0.150 mg S per 50 ml final solution were measured in 20 mm glass cells at different wave lengths and standard deviation calculated.

Wave length mμ	Standard deviation %
330	2.2
350	2.3
370	2.6
400	2.6
420	2.5
450	2.9
500	3.5
550	3.6

The relative standard deviation thus increases at increasing wave length in accordance with the theory presented.

Double determinations for the same conditions and lengths were made with a gelatine solution of varying age. When the trial was stopped after 1 month no change had been observed.

Extinction measurements in quartz cells at varying sulfate concentration and light wave length. Since an extinction maximum was expected at a wave length below the Beckman B range, further measurements were made with a Beckman

DU using 10 and 20 mm quartz cells. Owing to light absorption in the suspending medium itself, measurements below 240 mμ were impossible and in fact it has an absorption peak already at 270—280 mμ. This resulted in a marked peak on the extinction curves obtained with 20 mm cells but not on those obtained with 10 mm cells.

At decreasing wave length the linear range of extinction *versus* sulfate concentration diminished considerably, and was too small for practical purposes. Thus since Lambert-Beer's law was not valid here, the theory of optimum measuring wave length could not be satisfactorily verified.

CONCLUSIONS

Some results have been obtained which are in accordance with the presented theory of optimum measuring wave length; however, it could not be satisfactorily verified when applied to barium sulfate dispersions in a gelatine solution. The standard deviation is almost the same in the 330—420 mμ region but increases at longer wave lengths. The sensitivity increases with decreasing wave length. At the same time, however, the validity region of Lambert-Beer's law is decreased. An adequate compromise therefore seems to be a wave length of about 420 mμ, where determinations may be carried out within the range 0.05—0.20 mg S per 50 ml of final solution. Preferably, concentration and cell size is selected so that an extinction of 0.3 to 0.5 is obtained. For that reason a 50 mm cell is well suited. With these specifications 12 equally prepared solutions showed a standard deviation of 1.5 %.

Acknowledgement. Sincere thanks are due to Mr Kornél Horváth, who with great care and interest carried out all the measurements.

REFERENCES

1. Krober, O. A. and Howell, R. W. *J. Agr. Food Chem.* **6** (1958) 591.
2. Toennies, G. and Bakay, B. *Anal. Chem.* **25** (1953) 160.
3. Gassner, K. und Friedel, H. *Z. anal. Chem.* **152** (1956) 420.
4. van de Hulst, H. C. *Light scattering by small particles*, John Wiley & Sons, New York 1957.
5. Lewis, P. C. and Lothian, G. F. *Brit. J. Appl. Phys. Nottingham Conf. Suppl.* 1954, p. 71.

Received February 5, 1960.