

DESIGN OF A SIMPLE LASER SYSTEM FOR NEPHELOMETRIC DETERMINATION OF ANIONS

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Abstract

A simple analytical system suitable for nephelometric measurements is introduced in this article. The electronic and optical components are simplified so that the apparatus is easily assembled from materials that are generally available. This instrument is designed for the efficient measurement of anions, and microgram quantities of ions may be determined by a convenient method of titration. Using this system, the ion detection is performed on several species, and the preliminary results are reported here. The results from the determination of sulfate and chloride ions show a good detection limit (10^{-5} M), and a linearity range of 10^{-5} - 10^{-3} M.

Introduction

Determination of anions by using conventional methods, such as spectrophotometry, atomic absorption and emission, is difficult, hence other methods should be considered for their study. Turbidimetry and nephelometry techniques offer some advantages in this respect, therefore it was planned to use the turbidity effect for ion measurements. However, most of the instruments described in the literature are designed for turbidimetry [1-3], and only a few designs for nephelometric experiments are available [4].

In most reported cases, photometers or fluorometers are adapted for use as a nephelometer in the experiments [5]. For this reason, a simple and precise experimental method for nephelometry is developed in this work. Since the well-established commercial systems for nephelometric experiments are not easily accessible in every laboratory, the reported system can play an important role for these kinds of measurements with minimum costs and operational efforts. The proposed apparatus can also be modified for use in turbidimetry.

Turbidimetry and nephelometry involve the formation

of a suspension and the measurement of the ability of the suspension to absorb (T) or scatter (N) light. The use of these methods is suitable for the determination of those elements which do not give good color reaction or which give precipitates that are difficult to separate from their mother liquors. The analysis is most sensitive for very dilute suspensions. The intensity of the scattered light depends upon the number and size of the particles in suspension and, provided that the average size of the particles is fairly reproducible, analytical applications are possible. However, if the cloudiness or turbidity is to be reproducible, the utmost care must be taken in sample preparations.

We report the details of the design, construction, and operation of a simple nephelometric system. An apparatus for the performance of titration is also described and some of the fundamental factors limiting the accuracy of the system are discussed. The analytical method reported here is a precise, rapid and simple one for the determination of ions within the concentration range of 10^{-5} M to 10^{-3} M. The instrument can also detect signals produced by a pulsed light source, without a real need for a complicated system of detection such as a lock-in-amplifier or boxcar averaging

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and integrating modules.

Experimental Section

The block diagram of the apparatus used in this work is shown in Figure 1. A laser scattering system is arranged at right angles to the direction of the incident light to measure the intensity of the dispersed laser light from a turbid solution. The instrument uses a low power (0.5 mW) He-Ne laser at 632.8 nm wavelength. The low power has the advantage in that it reduces the heating of the sample which may produce an error in measurements. For a similar reason, the laser beam is directly incident on the sample solution without using any focusing optical element.

The signal detection system consists of a light collecting assembly and light sensitive detector. In addition, for processing the electrical signal, an amplifier and a suitable read-out device or a recording unit are also considered as shown in Figure 1. The optical design of the apparatus is simple and in principle functions similar to those reported for other light collection experiments. The scattered light from the nephelometric sample is incident on a camera lens, (Zenit f # 2), which collimates the beam, and a second camera lens, (Zenit f # 3), which matches the monochromator optics, focuses the beam onto the entrance slit of a monochromator (25 cm Jarrell Ash.)

After passing through its exit slit, the throughput light of the monochromator enters a photomultiplier tube (PMT) that is tightly connected to the unit. The scattered photon flux is then converted to an electrical signal by the tube and the resulting electrical signal is transmitted to the amplifier input. The amplified signal is then monitored by a digital voltmeter or can be recorded on paper by a chart recorder system.

Diffusion and scattering by different optical elements, sample cell and the room light are the main sources of the stray light in detection. The purpose of using the monochromator is to reduce the stray light level in order to obtain high spectral purity in scattered light from the sample. This monochromator rejects the stray light considerably and provides a very low level noise signal, as a result the signal to noise ratio is greatly improved. High stray light rejection of about 10^{-5} at 8 nm, far away from the 632.8 nm He-Ne laser line, is estimated by using such a monochromator. The output luminosity of the monochromator is proportional to apparent slit height, to grating surface area, and to the width of the smallest of the entrance or exit slits.

The bandpass and the resolution of the detected spectrum is also controllable by the instrumental line profile of the monochromator. For a slit width of 0.05 mm, the bandpass is about 0.2 nm for the He-Ne laser line when a 1200 gr/mm grating is used. As a result, stray light rejection and bandpass controlling are the two main reasons for adding

the monochromator to our detection system.

The general features of the electrical components and circuit design of the amplifier system built for this experiment are elaborated in Figure 2 and Figure 3. A simple high voltage power supply for anode of PMT is shown in Figure 2. A d.c. voltage of nearly -1kV is obtained by the tripler cascade from 220 V input, and is then stabilized by Zener diode to -564 V. This small power supply is built in the same package used for the detection system in such a way that introduces a little bit noise in detection signal.

Our detection system can process pulsed or d.c. signals for data acquisition. In pulsed mode, the signal intensity is generally lower but because of d.c. background noise elimination offers a better signal to noise ratio and more reproducible results. For d.c. mode, the PMT output signal is buffered by a low noise operational amplifier (LM 308) and is connected to a digital voltmeter (Fluke 8800), or a

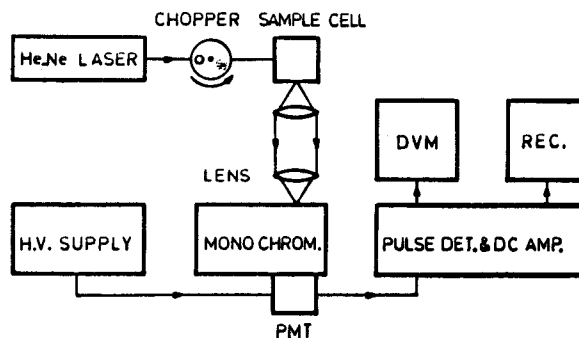


Figure 1. Block diagram of the laser system for nephelometric measurements

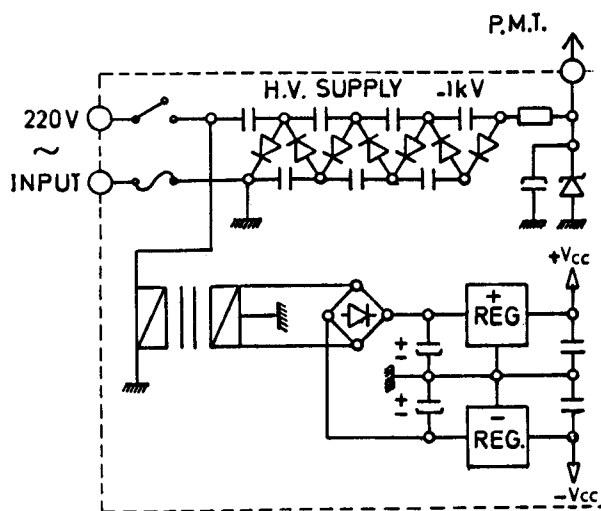


Figure 2. Schematic diagram of the power supply circuit

chart recorder (Fig. 3). A built-in A/D converter (L 7107) is also provided in the unit as an extra read-out with zero adjustment for background corrections, not shown in Figure 3.

A mechanical chopper in the laser beam allows the use of the pulsed detection technique that can result in an increase in the stability of the measurements [6]. In this mode, the PMT chopped pulse after buffer, A1, (Fig. 3) is amplified by an inverted operational amplifier A2 whose gain is selectable by the multiswitch S1 (gain of 0.1 to 100).

The capacitor C2 and R5 eliminate the d.c. level by derivation operation. The positive and negative needle pulses are therefore produced. Active peak detector (A4) stores the negative peak height of the amplified signal as a negative charge in the capacitor C3 which is already discharged by the positive needle pulse via A3. The charge is saved until the next pulse is sampled. Buffer A5 helps to read the real voltage of C3 without any change that can be made by the load of read-out unit, and finally the average of pulse heights will be read by a digital voltmeter (built-in or external).

System Performance

The operational performance of the system is tested using the experimental arrangement of Figure 1 for some ion measurements. Data acquisition requires the preparation of a nephelometric suspension and measurement of the scattered light from the precipitated particles in the solution. In the first experiment, the sulfate ions were detected by using this method.

A 0.100 M titrisol solution of H_2SO_4 (MERCK 9984) is used as stock solution for sulfate ion which is diluted with the proper amounts of triply-distilled water to produce standard sulfate ion, from 10^{-5} up to 10^{-3} M. By adding proper amounts of pure crystalline $BaCl_2$ (MERCK-1719) to ion solution in the presence of conditioning solution, the sulfate ion is precipitated. The conditioning solution contains 30 ml of concentrated HCl, 100 ml of 95% ethanol, 50 ml glycerol, 75 g NaCl dissolved in 300 ml of triply-distilled water. After 1 minute stirring (at a constant speed of 400 rpm) and waiting for 4-5 minutes, the uniform suspension of $BaSO_4$ is formed [7]. As stated in reference [7], the viscosity and surface tension of glycerol, ionic strength resulting from NaCl and pH adjusted by HCl, gives the conditions for new nucleus production instead of the growth of crystals which leads to a uniform suspension.

For chloride measurements, a 0.100 M NaCl titrisol (MERCK-9945) is used as the initial stock solution. Standard solutions between 10^{-5} to 10^{-3} M are prepared by diluting the stock solution with the proper amounts of triply-distilled water. Fresh 0.1000 M $AgNO_3$ titrisol (MERCK-9990) is used as the precipitating agent, and also for preparing 2×10^{-3} M titrant. Concentrated HNO_3 is used

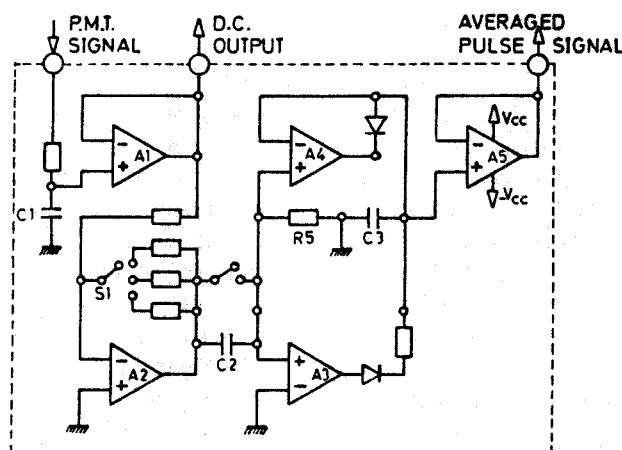


Figure 3. Schematic diagram of the detection system

as the conditioner in order to prepare a solution of uniform suspension.

Special care must be taken to avoid dust getting into the solutions. In the case of chloride, fast operation in darkness is also needed to avoid photochemical effects. For this purpose, all the vessels are blackened. The intensity of the scattered light depends upon the number and the size of the particles suspension, so the average size of particles should be uniform for analytical detections. The precipitate must also be fine, so as not to settle rapidly.

Since the relationship between the optical properties of the suspension and the concentration of the disperse phase is, at best, semi-empirical, a calibration curve or a titration means [8,9] is needed for nephelometric determinations. For our initial experiments, the calibration curve is constructed as shown in Figure 4.

For the construction of the calibration line for SO_4^{2-} and Cl^- , 3 ml of the suspension is transferred to a rectangular cell ($1 \times 4 \times 1$ cm³), and the scattered light is detected [10]. Figure 4 shows the scattered signal versus different sulfate concentrations. The linearity is very good in the range of 2×10^{-5} - 5×10^{-3} M. Since no precipitation is formed below this range, the ion signal remains almost constant. Our detection limit is 2×10^{-5} M which is limited by the solubility of $BaSO_4$ (K_{sp}). The background signal is due to the scattered light from the blank solution and the cell walls.

The calibration line for chloride for the concentration of 0.1×10^{-4} M is shown in Figure 5. A good linearity diagram is achieved for this range, and the detection is limited to 2×10^{-5} M for this measurement. The weakness of the method is that for the concentration above 10^{-4} M, a coagulation of suspension occurs which destroys the linearity diagram.

Because of the sensitivity of the $AgCl$ in intense light, the red light of the laser is used, and the light is chopped to

short pulses by a mechanical chopper. The chopping rate is about 1000 rpm which makes the reaction time about 0.15 ms. The chloride is measured by this pulsed method and the result is shown in Figure 6. In comparison to Figure 5 (d.c. detection), the pulsed method offers a better precision and linearity in the Cl⁻ determination. Between the range of 2×10^{-5} to 9×10^{-5} M the linear regression for correlation factor in pulse mode is 0.9968, in contrast to 0.9923 for d.c. detection. The accuracy of the results shown in Figure 6 is about 2% in comparison to 4% in Figure 5.

In the second attempt, a titration method is used for the determination of the chloride. For this purpose, 10 ml of the 2×10^{-4} M of Cl⁻ is transferred to a glass cell ($2.5 \times 2.5 \times 5$ cm), and is titrated with 2×10^{-3} M solution of AgNO₃ from a microburette with the resolution of 0.01 ml. During titration, stirring is done at a constant speed with a homemade miniature magnetic stirrer. Titration takes about 1 minute, and the signal measurement is performed during this period. Since in the titration method, the interference from the difference between sample and standard matrixes is eliminated, the nephelometric titration is examined by this set-up. The result from titration is presented in Figure 7. A sharp equivalent point is achieved which results in an accuracy of about 2% in measurements.

In comparison with other methods, it must be pointed out that determination of chloride and sulfate ions is difficult by using the conventional method of atomic and emission spectroscopy. No emission method for sulfate ions alone has been reported so far. The emission method for chloride ions encounters difficulties because of the fact that its emission line is in the VUV region of the spectrum.

However, the potentiometric method based on ion

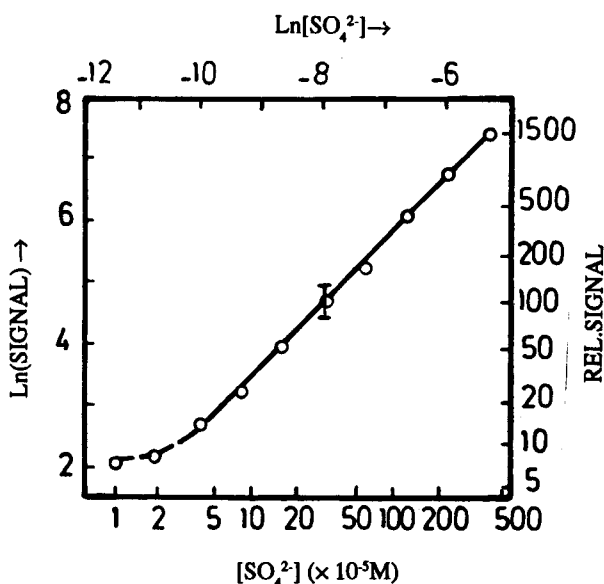


Figure 4. Graph of calibration curve for sulfate measurements

selective electrodes and titration is one of the few methods that can be implemented for such ion determination. Even though ion selective electrodes can detect such ions, at the same time it is also sensitive to other ions which might cause some interference in measurements. This effect is more pronounced when the analyte is diluted to a concentration of about 10^{-5} M. The ion selective method is also sensitive to temperature changes which might cause error in measurements. The classical titration methods for sulfate and chloride ions have proved to be effective at high ion concentration and have a low detection limit of the order 10^{-3} M.

The reported nephelometric and nephelometric titration

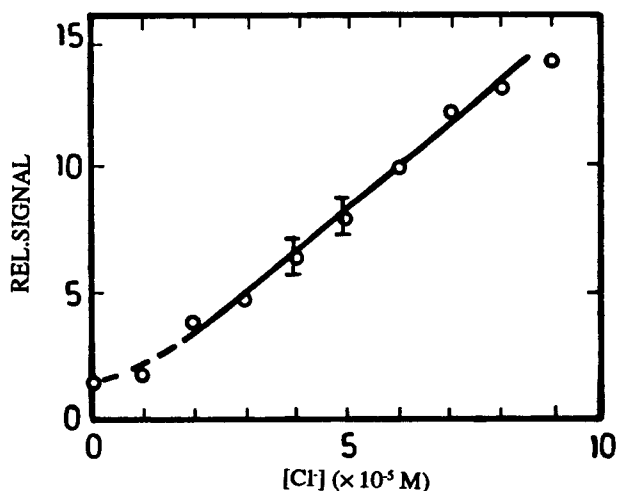


Figure 5. Nephelometry signal of chloride at different concentrations

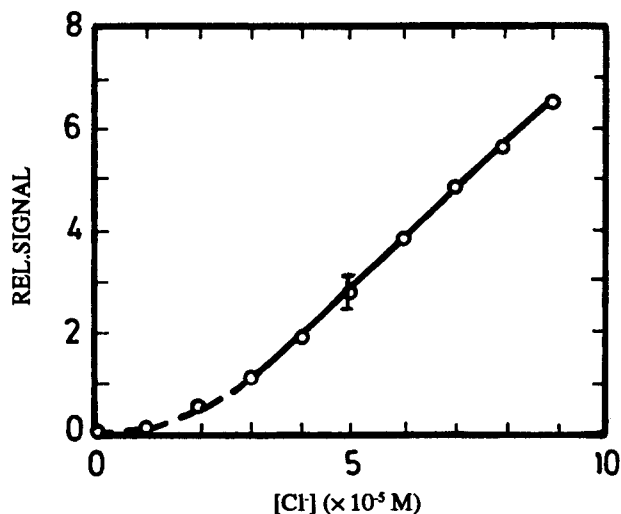


Figure 6. Nephelometry signal of chloride by using a pulsed detection scheme

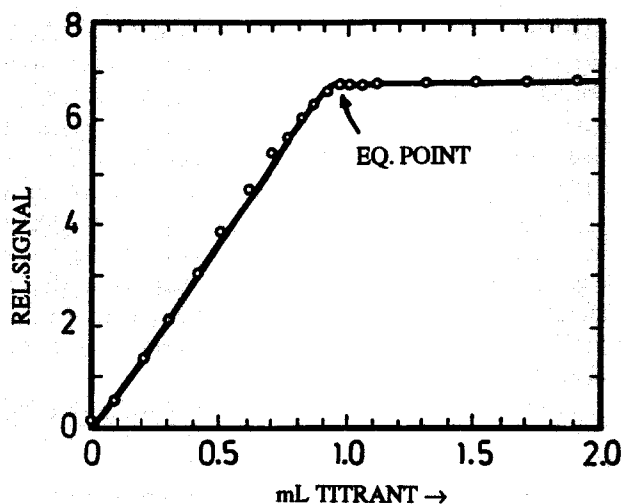


Figure 7. Titration curve of 10 ml 2×10^{-4} M chloride with 2×10^{-3} M AgNO_3

methods are therefore suitable for anion measurements in the 10^{-5} M range. It is a simple, relatively fast method, and in contrast to the turbidimetric method, the sensitivity of the method can be increased by increasing the intensity of the laser light source. The detection limit mainly depends on the solubility condition of the precipitate. In comparison with the other nephelometric experiments [4], our system, in spite of its simplicity, shows a comparable detection limit (10^{-5} M) with good precision (2%).

Conclusion

The first result of this work is the introduction and successful application of a new laser system for nephelometric measurements. The reported system shows a good performance for anion determination which is comparable with the most advanced commercial instruments in spite of its simplicity and low cost. The second point to make is that the electronic detection unit is designed so that both pulsed and d.c. signals can be easily processed. The versatility of the system permits the easy replacement of the light source, optical collection assembly,

and sample compartment according to experimental needs. These advantages allow one to study, for example, titration method, scattering at different wavelengths, and multiple sample uses. The system can also be modified in order to be effectively converted for fluorescence and turbidimetry measurements.

Application of the reported set-up in the determination of small amounts of chloride and sulfate ions has shown a relatively good sensitivity, accuracy, detection limit and a wide linear dynamic range. Considering the importance of the analysis of chloride and sulfate ions in the water of power plants, this method can be implemented for routine determination of samples having small amounts of the mentioned ions.

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