

## Determination of Chloride by Gas-Phase Molecular Absorption Spectrometry

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(Received 27th July, 1989, revised 17th October, 1989)

**Summary:** Chloride in the range of 0.1 to 0.5 mg is determined by gas-phase molecular absorption spectrometry. Chloride samples were quantitatively oxidized by successive addition of potassium persulphate solution and sulphuric acid. The released chlorine gas was swept in stream of nitrogen through a long-path optical cell where its absorption was measured at 330 nm. Various parameters concerning the determination have been investigated and chloride content in a number of samples was determined by the described procedure.

### Introduction

Gas-phase molecular absorption spectrometry, GPMAS, as a quantitative analytical technique was for the first time used for the determination of sulphur dioxide [1]. Later on the technique was employed for other sulphur and nitrogen containing compounds and ions like sulphide [2], sulphate [3], nitrate [4], cyanide [5] and urea [6]. Recently the range of its applications is extended to the estimation of halogens [7,8]. In GPMAS a gas resulted from a chemical reaction is usually passed through a long-path optical cell and absorbance at a certain wavelength is measured. The technique is relatively less sensitive, but its simplicity, precision, speed and relative ease of automation is comparable with any other alternative method. As far as instrumentation is concerned, an atomic absorption spectrometer after replacing the flame assembly with an optical cell and using a continuous source, can be used for GPMAS. Alternatively the optical cell can be fitted in the light path of a single or double beam UV/VIS spectrophotometer. In the work described here, chloride at 50 to 500 micro gram level is determined by quantitative oxidation of sample with persulphate solution and sulphuric acid. The released chlorine gas is passed through an optical cell where its absorption is measured at 330 nm. Various parameters like gas flow rate, choice of oxidant and reaction volume and interferences due to other ions have been investigated. A number of chloride containing samples are analysed by the described procedure as well as by a reference method [9].

### Experimental

#### Apparatus

The apparatus used for the oxidation of chloride sample is shown in Fig. 1. Potassium persulphate solution and sulphuric acid were added successively from reservoirs to the sample tubes. Sample tubes were 8x2 cm Pyrex tubes with B 19 quickfit sockets which made them easily interchangeable. The evolved chlorine gas from chloride sample was passed through a 10x1 cm glass cell with quartz windows with the help of plastic tubings. The cell was placed in the light path of a SP 8-400 UV/Vis Spectrophotometer. Absorption signals were recorded on a Perkin Elmer 561 recorder.

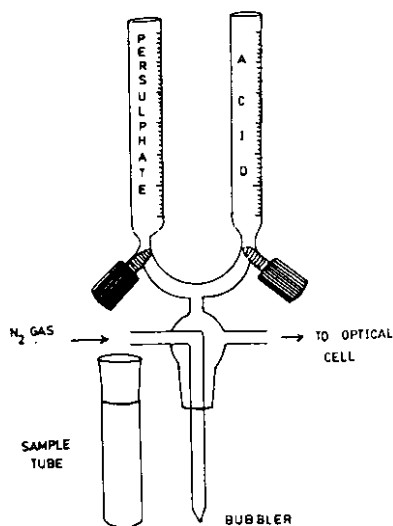


Fig. 1: Apparatus for Chlorine Generation

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### Reagents

To prepare  $1000 \mu\text{g ml}^{-1}$  solution of chloride  $1.647 \text{ g}$  of sodium chloride was dissolved in deionized water and diluted to one litre. The oxidizing reagent was a saturated solution of potassium persulphate in  $3.6 \text{ N}$  sulphuric acid to which a trace of silver nitrate had been added. AnalaR grade  $36\text{N}$  sulphuric acid was used for oxidation alongwith persulphate solution.

### Calibration

Set up the apparatus and fill the reservoir with persulphate solution and sulphuric acid. Fit an empty sample tube on the bubbler and pass a stream of nitrogen until a stable base line on the recorder is obtained. Transfer  $0.1\text{--}0.5 \text{ ml}$  aliquot of  $1000 \mu\text{g ml}^{-1}$  chloride solution into another sample tube with the help of an Agla micrometer syringe. Remove the empty tube from bubbler and fit the tube containing chloride sample. Run in  $2 \text{ ml}$  of persulphate solution and then  $3 \text{ ml}$  of concentrated sulphuric acid from their reservoirs. After about ten seconds an absorption signal due to evolved chlorine appears on the recorder. Wash the bubbler with deionized water after every chloride sample.

### Results and Discussion

#### Calibration and Precision

A slightly curved calibration for the range  $100\text{--}500 \mu\text{g}$  chloride has been obtained by described procedure. A lower range of calibration could also be obtained by using a smaller optical cell, reducing the dead volume, increasing the gas flow-rate and damping the recorder noise. Use of a hot reaction vessel also improved the detection limit of chloride. Precision of the method has been checked by taking ten repeated measurements of  $100 \mu\text{g}$  of chloride. The recorder peak height showed  $2.5\%$  relative standard deviation which corresponds to  $3.2 \text{ g}$  of chloride. Defining the detection limit that concentration of chloride which gives a signal three times of the size of the standard deviation, detection limit of  $10.5 \mu\text{g}$  of chloride was obtained.

#### Effect of Gas flow-rate and Slit Width:

Effect of gas flow rate on the signal height was checked by varying the flow rate of carrier gas

from  $0.75 \text{ lit/min}$  to  $2 \text{ lit/min}$  with the help of a manometer. By increasing the gas flow rate there was significant increase in the peak height. However the peaks obtained at slower flow rate were relatively broad than those obtained at slow rates which indicated that the area of the peaks was constant. This was confirmed by the constant weight obtained when the peaks of different heights were cut down from chart paper and weighed.

Effect of slit width on signal height was checked by changing the slit width of different levels. No considerable effect on signal height has been observed when repeated absorption measurements of  $100 \mu\text{g}$  chloride were taken at  $0.5 \text{ nm}$ ,  $1 \text{ nm}$ ,  $2 \text{ nm}$ , and HE (High Energy) positions of slit width control of the instrument.

#### Effect of potassium Persulphate Solution Volume

To get the maximum absorbance signal of chloride sample effect of volume of saturated potassium persulphate solution was checked. As shown in Fig. 2, the maximum signal was obtained when  $1.5\text{--}2 \text{ ml}$  of the persulphate solution was used alongwith  $3 \text{ ml}$  of sulphuric acid. Less than  $1.5 \text{ ml}$  of the solution yielded smaller signals probably due to the fact that the amount of persulphate solution was not enough. Similarly increase in the volume of persulphate solution also decreased the signal height. This was due to the increase in total volume of the reaction mixture which entrapped the liberated chlorine.

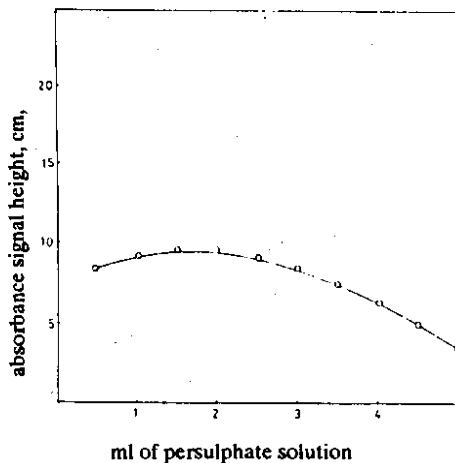


Fig. 2: Effect of Persulphate solution volume

### Effect of Sulphuric Acid Volume and Concentration

Keeping the volume of persulphate solution constant i.e., 2ml, the volume of 36 N sulphuric acid was changed to get the optimum volume of acid. As shown in Fig. 3, best absorbance signals were obtained when 3-4 ml of acid was used. Lesser volumes of acid gave smaller signals due to insufficient amount of acid. Signal height was also reduced when more than 4 ml concentrated acid was used. This was again due to the increase in total volume of the reaction mixture which entrapped the significant quantity of liberated chlorine. Effect of the strength of sulphuric acid was also checked by using the equal volume of acid but of different strengths. The effect of acid strength is shown in Fig. 4.

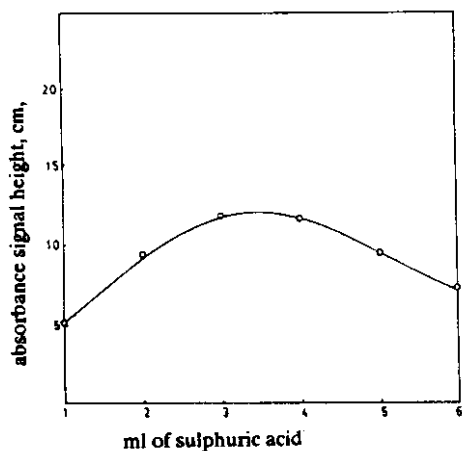


Fig. 3: Effect of sulphuric acid volume.

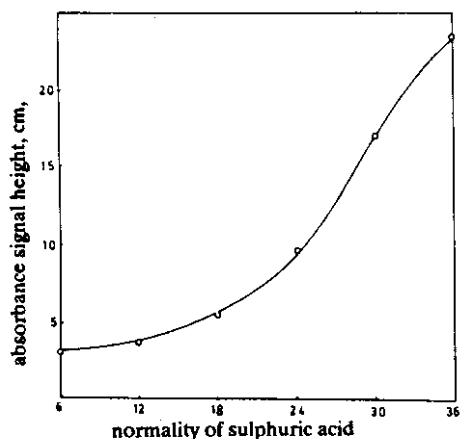


Fig.4: Effect of acid strength.

It has been found that the reaction is highly dependent upon the strength of sulphuric acid. The acid less than 30 N gave negligible results. The reaction was slow and almost non-significant amounts of chlorine were liberated with relatively dilute acids. The maximum amount of chlorine was liberated and a sharp signal was produced when the most concentrated acid i.e. 36 N was used.

### Effect of Total Volume

Effect of total volume of the reaction mixture was checked by diluting the mixture with water.

Increase in total volume had an adverse effect on the absorbance signal. The signal obtained with 5 ml reaction mixture was almost double than that obtained with 10 ml of the total volume. This was mainly due to the fact that a larger volume of reaction mixture retarded the oxidation of chlorine and reduced the signal height.

### Effect of other Ions

Effect of some other common ions has been checked on the determination of chloride by the described procedure. Chlorine samples each containing 100  $\mu\text{g}$  chloride, were analysed along with other ions present in equimolar concentrations. The results obtained are summarized in Table-1. As

Table 1: Effect of other Anions on the Molecular Absorption Spectrometric Determination of Chloride

Anion	100 $\mu\text{g}$ of anion added as	Chloride found, $\mu\text{g}$
Sulphate	Sodium	103
Sulphite	Sodium	102
Acetate	Sodium	98
Nitrate	Potassium	82
Iodide	Potassium	75
Oxalate	Potassium	99
Carbonate	Sodium	100
Bromide	Potassium	82
Nitrite	Potassium	85
Thiosulphate	Sodium	101

Chloride taken 100  $\mu\text{g}$  as sodium chloride

Table 2: Comparison of Results for Analysis of Some Chloride Samples

Samples	Chloride found $\mu\text{g/ml}$		
	by Describedb Method	by Conductometric Titration	
A. Brine solutions from soda plant (1000 times diluted).			
i)	2D <sub>4</sub>	255	248
ii)	2D <sub>5</sub>	198	205
iii)	2D <sub>6</sub>	252	258
iv)	2D <sub>7</sub>	220	232
v)	2D <sub>12</sub>	195	202
B. Pharmaceutical suspensions containing ammonium chloride			
i)	Ammodyl (100 times diluted)	198	195
ii)	Pulmanol (20 times diluted)	235	245
iii)	Tuscolin (100 times diluted)	260	263
iv)	Benadryl (100 times diluted)	258	260
v)	Hydrylin (20 times diluted)	298	310

it is shown by the Table, the presence of sulphate, sulphite, acetate, oxalate and carbonate did not cause any significant effect on the chloride determination. However, nitrate, nitrite, bromide and iodide interfered the determination considerably and yielded low results. This was probably due to the fact that these ions retarded the liberation of free chlorine from chloride sample. Reduction of chlorine back to chloride as an interhalogen compound is also possible because iodine and bromine are produced when iodide and bromide ions are present alongwith chloride sample.

#### Determination of Chloride in Samples

The proposed method of gas phase molecular absorption spectrometry was applied to the determination of chloride ions in several pharmaceutical preparations. The results obtained were then compared with those obtained by potentiometric titrations [9]. As it can be seen in Table-2, there is a good agreement between results obtained with two methods. The samples containing higher concentrations of chlorides have to be appropriately diluted

prior to analysis. A few samples of brine solution obtained from a local caustic soda plant have also been analysed by the described procedure as well as by the reference method [9].

#### Conclusion

The present method for the determination of chloride, based on the molecular absorption of chlorine evolved from the sample is though less sensitive than other instrumental methods but its simplicity, speed and ease with which the method could be automated are far greater than any other method used for this purpose. Better sensitivity can also be achieved by reducing the volume of optical cell and by using a trap system or signal modulation. The most promising features of the method are its speed and ease of automation. With optimum carrier gas flow-rate a measured chloride sample can be quantitatively analysed in thirty seconds. Similarly by making suitable changes in the instrumentation, the procedure can be easily converted into a fully automatic method for chloride determination.

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