STUDIES

IN

MICRO ANALYTICAL

METHODS.


By

THOMAS HUME CAULFIELD, B.Sc.


Thesis
presented for the Degree of
Doctor of Philosophy,
Glasgow University


The University,
Glasgow.

<p style="text-align:center;">CONTENTS.</p>

# INTRODUCTION.

This thesis consists of studies in the micro-analysis of organic compounds. The problems involved are, for the most part, accurate determinations of small amounts of inorganic products. The analyses have been done wherever possible by volumetric means.

The work is presented in four sections:-

(1)     Simultaneous determination of sulphur and halogen by combustion, involving the estimation of the total acidity due to sulphur and halogen acids, and obtaining the halogen content by the reactions outlined as follows:-

$$2NaCl + 2Hg(OH)(CN) \rightarrow 2NaOH + Hg(CN)_2 . HgCl_2$$
$$(Vieböck)[1]$$
$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$
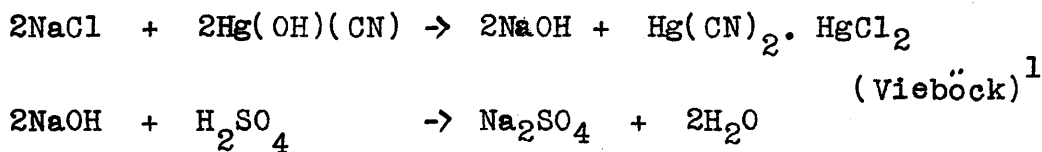
Sulphur was calculated by difference.

(2)     Determination of sulphur in compounds containing sulphur, nitrogen and halogen.

The conditions under which sulphur is most favourably oxidised to sulphur trioxide (for $H_2SO_4$), are not conducive to the liberation of combined nitrogen either completely as molecular nitrogen or completely as nitrogen peroxide. Hence the total acidity realised by combustion is always short of the theoretical for all three elements. The analysis for the sulphur content, therefore, necessitated

the development of a new process.

Friedrich[2] proposed a method of overcoming this, but when tested it was found to be unreliable, and after investigating the possibilities of various methods, that outlined by the following steps

$$Na_2SO_4 + xBaCl_2 \rightarrow BaSO_4 + 2NaCl + x-1 \; BaCl_2$$
$$BaCl_2 \rightarrow BaCrO_4 \rightarrow I_2 \rightarrow Na_2S_2O_3$$
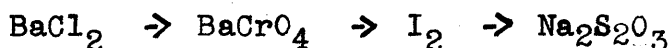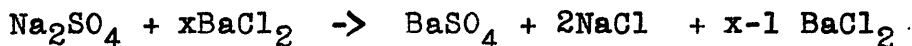
was satisfactorily applied to micro-analysis.

(3)     Sources of error encountered during the attempted repetition of a recently published method for micro-methoxyl determination were traced and eliminated satisfactorily.

The reaction involved:-
$$CH_3OR \rightarrow CH_3I \rightarrow CH_3IBr_2 \rightarrow IBr \rightarrow HIO_3 \rightarrow 6I \rightarrow 6Na_2S_2O_3$$
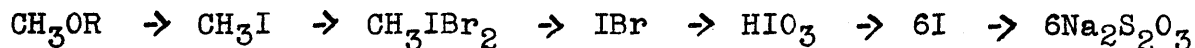
(4)     The satisfactory manner in which compounds were decomposed for the sulphur-halogen determination (section 1) led to attempts being made to use the same tube filling, viz. platinum-rhodium gauze instead of Pregl's[3] universal filling for carbon and hydrogen.

Excellent results were obtained for compounds containing carbon, hydrogen and oxygen, and a new method for eliminating the effect of oxides of nitrogen on the carbon-hydrogen determination, using this filling, gives promise of being practicable.

(1)   The Determination of Sulphur and Halogen in Organic Compounds.

The determination of sulphur in organic compounds free of nitrogen and halogen may be effected by the method and apparatus described by Pregl[4]. An aqueous solution of perhydrol is used as the trapping agent for the oxidised sulphur. Sulphur trioxide mainly is produced during the combustion, but any dioxide which is formed is readily oxidised to the trioxide by the perhydrol.

According to Kneitsch[5] the state of oxidation of sulphur depends on the temperature at which this takes place.

The following figures illustrate the equilibrium of Kneitsch Sulphur Dioxide-Trioxide System.

| Temp. °C. | | $SO_3$ Per cent. | Temp. °C. | $SO_3$ Per cent. |
|---|---|---|---|---|
| 300) | Equilibrium | ( 76 | 500 | 96 |
| 350) | not attained | ( 95 | 550 | 88 |
| 400 | | 100 | 600 | 80 |
| 450 | | 99 | | |

It is obvious that the least demand is made on the perhydrol if the temperature of the oxidising atmosphere is between $400°$-$450°$C. Accordingly the temperature of the catalyst should be maintained within these limits.

Pregl found difficulty in combining the estimations of sulphur and chlorine (halogen), although he suggested separate methods for each[4,6].

Vieböck[7] successfully employed perhydrol in the determination of chlorine and bromine.
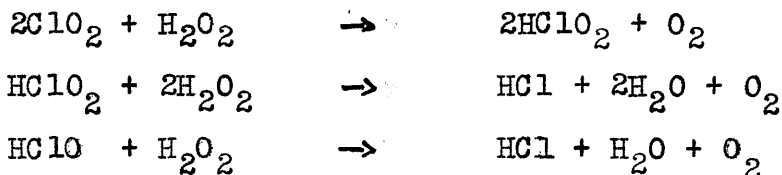
Cowie and Gibson[8] following on, combined the estimation of sulphur and halogen, by using perhydrol and altering the

apparatus slightly by affixing to the bead tube an adaptor-like section containing a glass spiral moistened with alkali and per-hydrol solution, and dipping into a conical flask.

The determination of sulphur and chlorine was done by combination of total acidity, - chlorine (Cl) by Volhard's method - and hence sulphur by difference.

During the combustion of halogen containing substances an oxide of chlorine is formed which normally escapes out of the system.

Perhydrol has the effect of reducing the oxides of chlorine (and the oxyacids) to hydrochloric acid, according to the equations:-

$$2ClO_2 + H_2O_2 \longrightarrow 2HClO_2 + O_2$$
$$HClO_2 + 2H_2O_2 \longrightarrow HCl + 2H_2O + O_2$$
$$HClO + H_2O_2 \longrightarrow HCl + H_2O + O_2$$

The experimental difficulty of the method proposed by Cowie and Gibson[8] for the halogen determination is the observation of the end point.

Further experiments having failed to improve the definiteness of this end point, other methods of determining halogen were explored (page 29).

Mohr's[10] method for estimating halogen has one advantage over Volhard's[9] in that it is based on the direct titration of halide with standard silver nitrate solution. The end point is noted when there is formed a reddish precipitate of silver chromate by the reaction of the first excess of silver ion with chromate ion added to the halogen solution as indicated.

Fajans and Frankenburger[11] have pointed out that estimations by Mohr's method tend to be high, which may be accounted for by the solubility of the silver chromate. Mohr's estimation cannot be conducted in acid solution, as can Volhard's,[9] and precipitation of the silver chloride is not so refined as in the thiocyanate method in consequence.

Investigations of this method for micro-analysis are detailed in the experimental section of this thesis, and show it to be insufficiently accurate.

## Potassium Cyanide as a quantitative reagent for Chloride determination.

Silver salts are characterised by an ability to form complex salts. Silver cyanide redissolves in potassium cyanide solution forming a complex according to the equation:-

$$AgCN + KCN \rightarrow K.\left[Ag(CN)_2\right]$$

Attempts were made to use this dissolution of the insoluble silver salts as a means for estimating the excess silver ion in the precipitation of chloride. They were unsuccessful and details will be found on page 33.

## Determination of excess Silver ion by Iodate ion.

Berend[12] has proposed the use of potassium iodate as a means whereby excess silver ion may be estimated and hence halogen. The solubility of silver iodate in water is too great for the method to be applicable to micro analysis.

In alcoholic solutions the solubility of the silver iodate

is considerably less than in aqueous solutions. Unfortunately silver sulphate is precipitated in alcoholic solution. The addition of nitric acid to the alcoholic solution prevents the latter salt coming out of solution, but the solubility of the silver iodate increases in this medium. The opposition of these factors leads  to the method being rejected.

## Mercuric Oxycyanide.

The solubility of mercuric chloride in water is very slight and in concentrated solution hydrolysis is negligible. Hence there have been proposed methods for halogens based on this fact.

Votoček[13] in 1915 proposed a method for titrating chloride solution with standard mercuric nitrate solution, using as internal indicator a dilute solution of sodium nitroprusside.  The end point was reached at the first opalescence.

Jureček[14] has applied this principle to estimation of small amounts of chloride and bromide with considerable success.

In support of the general principle of analysis of halogen content by precipitation of the mercuric halide comes Vieböck's[1] work on the determination of neutral chloride by an acidimetric method depending on the precipitation of the salt $Hg(CN)_2.Hg(Cl)_2$ according to the following :-

$$2Hg(OH)(CN) + 2NaCl \rightarrow Hg(CN)_2.HgCl_2 + 2NaOH$$
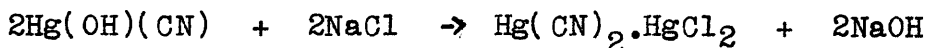
In the presence of excess neutral mercuric oxycyanide saturated solution the reaction goes completely towards the right with formation of sodium hydroxide equivalent to the chloride

present. This alkali may be titrated with sulphuric acid without interference with the balance of the equilibrium in concentrated solution.

This reaction is specific for halogens and depends on the well-known affinity of mercury for halogen. Special experiments with known solutions showed that their halogen content can be determined irrespective of added sodium sulphate.

Vieböck investigated this method for halogen analysis on a hemi-macro and micro scale, and he states, as has been above remarked upon, that the compound $Hg(CN)_2HgCl_2$ suffers practically no hydrolysis in concentrated solution, whilst the corresponding compound $Hg(CN)_2HgSO_4$ is strongly hydrolysed in comparison. Hence the usefulness of the salt $Hg(OH)(CN)$ in the present estimation.

In this work it was applied mainly to the estimation of chloride in the presence of sulphate. The balance of the reaction will go towards the left if the solution is a dilute one, hence the first consideration is the maintenance of conditions which promote quantitative formation of alkali.

If a saturated solution of mercuric oxycyanide be used to bring about the chemical change, then it is possible to estimate chloride without the dilution caused by the addition of the standard aqueous acid solution having any effect on the end point. Illustrations of this appear on page 35 of the experimental section. Analysis, successfully effected by this method, of 11 compounds will be found on page 40.

Section thro' SN.
(enlarged.)

$O_2$

(Scale, $\div \frac{1}{4}$.)
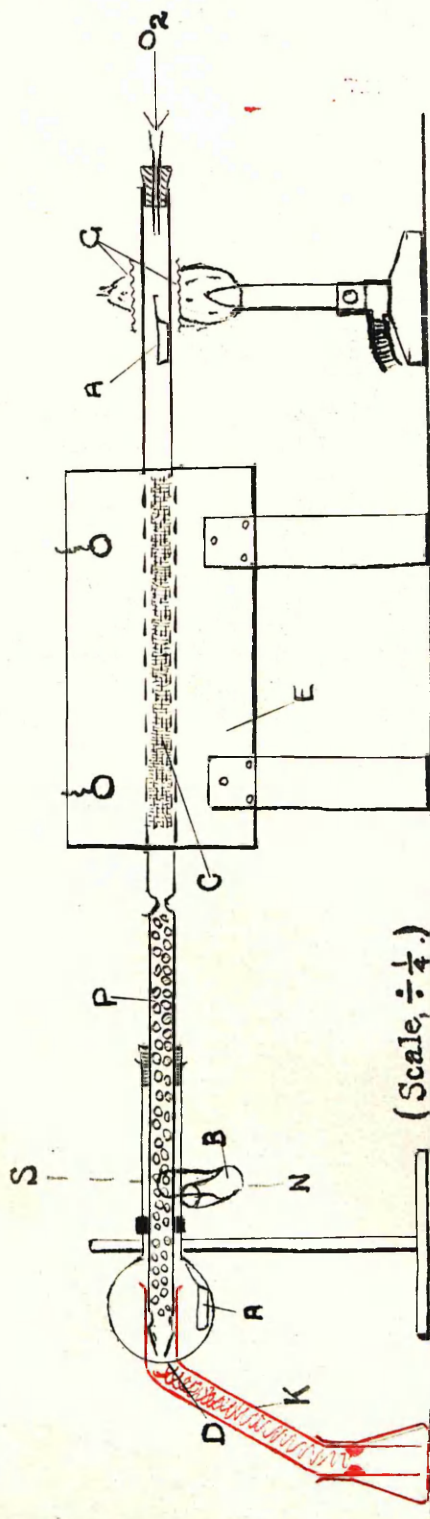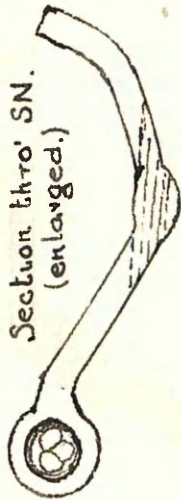
A. Platinum boat.
B. Bulb (reservoir).
C. Pt/Rh contact.
D. 50 Ml. distilling flask.
E. Electric furnace.
G. Gauze.
P. Bead tube.
K. Cowie's adapter system (in red ink).

A test tube was substituted for the distilling
flask in the Pregl system.

<u>Procedure</u>.

2-5 mg. of sodium carbonate is weighed into a small platinum boat which is introduced into a 50 cc. distilling flask, and dissolved in 0.5 cc. water. 0.04 cc. or thereabouts of perhydrol is added and this solution sucked into the beads of a clean dry combustion tube (the bead section is not thoroughly dry). The solution is retained in the beads, the flask affixed to the combustion tube by a thin rubber stopper and the combustion tube laid in position. The platinum-rhodium contact is now pushed into place in the combustion tube area heated by the furnace. 0.5 cc.$^N$/100 alkali solution and one drop of perhydrol are now pipetted into the side arm of the distilling flask and the whole apparatus assembled. The side arm of the flask is now tilted to a suitable position for the intermittent bursting of the seal to be obtained.

The stopper at the entrance to the tube is withdrawn and the weighed out compound, 3-5 mg. introduced in a platinum boat into the tube and pushed along about $\frac{12}{cm}$. from the entrance. The stopper is replaced and joints examined and tightened, and heating commenced about 7cm. from the entrance to the tube, with a bunsen burner. The bunsen is gradually moved along towards the compound, and this or a decomposition product of it, slowly distils before the heat into the furnace area    heated to $400^o$-$450^oC$.

The products issuing from this are trapped in the bead tube solution and in the distilling flask.

After burning  the substance, the tube is swept for some 20 minutes with oxygen, dismantled and cooled. The alkali-perhydrol partly spent solutions are now washed into the distilling flask

with 10-15 cc. water, and the solution titrated for total acidity allowance being made for any acidity due to the perhydrol. Methylene Blue/Methyl Red mixed indicator solution is used.

Thereafter the solution is transferred to an evaporating basin (silica) and the distilling flask thoroughly washed. The washings are added to the solution in the evaporating basin, and the whole concentrated under gentle heat on a muffle cone. The contents are evaporated almost to dryness in some 20-30 minutes, then 10 cc. of saturated neutral mercuric oxycyanide solution is added and the solution titrated with standard sulphuric acid for the halogen content. The sulphur is found by difference.

---

(2)   Determination of Sulphur in compounds containing Sulphur,
Halogen and Nitrogen.

Analysis of a sulphur-halogen-nitrogen-containing compound
by the combustion method as for sulphur and chlorine shows a total
acidity in excess of that required for the sulphur and chlorine
and short of that required by all three elements.

This "extra" acidity is due to the nitric acid formed by
the nitrogen of the compound according to the equations:-

$$N + O_2 \rightarrow NO_2$$
$$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$$
$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O$$
$$\left[ HNO_2 + HClO \rightarrow HNO_3 + HCl \right]$$
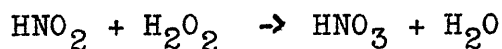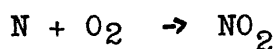
Tarvin, Todd and Boswell[15] assert that nitrous and hypo-
chlorous acids do not long exist in the same solution.  Hence the
bracketed equation.

Among methods tried for the analysis of sulphur (sulphate)
obtained by combustion were the following:-

1.)   Titration of sulphate with standard barium chloride
solution using rhodizonic acid as indicator.

Sodium rhodizonate in solution is yellow, whilst the
corresponding barium salt solution is red coloured.  Strebinger
and Von Zombory[16] made use of this in estimating sulphate volu-
metrically.  When the barium ion just  exceeds that amount
required by the sulphate, the red rhodizonate indicates the end

point of the titration.  This method was found to be serviceable
in $N/10$ solutions but the degree of sensitivity was not sufficient
when it was applied to $N/100$ solutions.  Hence the method was
rejected.

2.)  Tetrahydroxy quinone, allied to rhodizonic acid chem-
ically exhibits similar characteristics as an indicator.  This
substance was tried under conditions similar to those for rhodi-
zonic acid but it was also insufficiently accurate when applied
to $N/100$ solutions. This method proposed by Schroeder[17] has been
modified by Sheen and Kahler[18] since this work was completed with
a fair amount of success.  They are content with errors of from
1-4% and have added to the method the use of a side lamp adjacent
to the solution-containing vessel to increase the visibility of
the end point.

3.)  Benzidine hydrochloride was next considered as a
means of estimating sulphate.

This method, proposed by Muir[19], was applied by Fiske[20]
and Drummond[21] to determination of sulphate in biochemical solu-
tions.

The results with micro work were so inaccurate as not to
be worthy of note.

4.)  From Pregl's "Quantitative Organic Microanalysis"
English translation, 3rd edition, page 163, is culled the follow-
ing :-

"Friedrich has recently published a volumetric method of
determining sulphur in substances containing nitrogen and halogens.

Its essential features are that the combustion tube containing spirals moistened with perhydrol is rinsed into a quartz basin after the combustion, and the washings are then concentrated on the water bath until their volume is 10-15 c.c." This solution is neutralised."By this means all the acids are converted into their sodium salts. A quantity of sulphuric acid corresponding to the alkali already used, is then added, thus converting all the sulphuric acid formed during the combustion into the bisulphate, whilst the volatile acids can be driven off by evaporating to dryness. After warming the residue for half an hour on the water bath, it is dissolved in a small amount of water, after which the quantity of sulphuric acid corresponding to the amount of sulphur originally present is determined by a further titration with alkali."

Before attempting to repeat Friedrich it was discovered that if sodium sulphate solution is added to a solution containing sulphuric acid with nitric acid and/or hydrochloric acid, the solution may be evaporated to dryness with evolution of the volatile acids and complete retention of the sulphuric acid originally present.

Thus the three titrations of Friedrich are replaced by only one titration with the same result.

In applying Friedrich's method to combustion products in this work it was found that a deficiency of sulphur always appeared and it was concluded that this was due to incomplete oxidation of the sulphur to sulphur trioxide in spite of the temperature, and

that the remaining partially oxidised sulphur was lost as sulphur dioxide in company with the nitric and hydrochloric acids.

5.) The successful method was based on the following procedure :-

The sulphuric acid was neutralised and the alkali titration gave an indication of the barium chloride standard solution required to precipitate the sulphate.

This volume of standard $BaCl_2$ solution was exceeded slightly and the excess barium ion precipitated as chromate by addition of potassium chromate solution.

The combined precipitates of barium sulphate-chromate were filtered, and the chromate determined by adding acidified potassium iodide solution and titrating the liberated iodine with standard sodium thiosulphate solution. Hence the excess barium can be calculated and from that the amount required for sulphate.

Procedure.

 The procedure recommended for the determination of sulphur in organic compounds also containing nitrogen and halogen is as described in Pregl's Quantitative Organic Microanalysis, page 30 of the 3rd English Edition.

 After the combustion, the tube is washed out with about 10 cc. water, into a 100 cc. beaker. The acid solution is neutralised and the titration here gives the utmost volume of $BaCl_2$ standard solution required to precipitate the sulphate in the solution. The beaker with the neutralised solution is heated whilst this volume of barium chloride solution is run into it. The contents of the beaker are cooled, and an excess of potassium chromate solution added. The barium ion is at once precipitated as barium chromate.

 The combined precipitates of barium sulphate and barium chromate are now filtered free of other salts by an Emich[22] filter stick, and are washed with 50% alcohol. Upon addition of an excess of hydrochloric acid to the residue in the beaker and around the filter stick, chromic acid is liberated.

 The filter stick, which holds some of this acid inside the shank is now rinsed inside and out with water, and taken out of the beaker.

 Potassium iodide (a crystal) is now added to the acid solution and the liberated iodine titrated with sodium thiosulphate standard solution, using a dilute starch solution as the indicator.

This titration determines the excess barium ion present and therefore by difference the amount used for sulphate can be calculated.

## (3)  Micro-Methoxyl Determination.

The recent achievements of Viebök and Schwappach[23] in the determination of Methoxyl groups on a macro scale, and the application of their method to micro determinations by Viebök and Brecher[24] led to attempts being made to employ the method for routine micro methoxyl determination.

According to the above workers, when methyliodide, which is liberated from the alkoxyl containing body by reaction with hydriodic acid, is passed into a solution of bromine in acetic acid containing potassium acetate, the alkyl iodide reacts schematically thus :-

$$\left[ CH_3OR \rightarrow \right] \; CH_3I \; \rightarrow \; CH_3IBr_2 \; \rightarrow \; IBr \; \rightarrow \; HIO_3$$
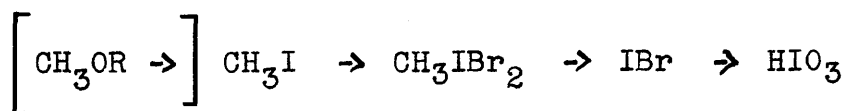
Upon addition to the above solution of sodium acetate, and formic acid, the excess of bromine is destroyed, and upon addition of potassium iodide and sulphuric acid, iodine is liberated according to the equation :-

$$HIO_3 + 5HI \; \rightarrow \; 3H_2O + 6I.$$
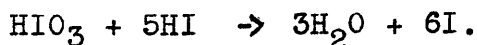
That is, for every methoxyl radicle present in the original compound there are liberated six iodine atoms which result in a six-fold titration and consequently heighten the accuracy of the determination. The titration is of sodium thiosulphate with a dilute solution of starch as indicator.

Arndt and Martius[25] employed this method in analysis of alkoxyl compounds containing sulphur and nitrogen, using weights of from 25-50 mg. substance. They found the method satisfactory.

Vieböck and Brecher used weights of from 1-5 mg. but on attempting to repeat this work a number of difficulties were encountered and after investigation of the boiling solution, and washing solution had been made these difficulties were finally traced to the absorbing solution.

In the experimental pages of this work are found details showing that the absorbing solution recommended by Vieböck and his co-workers is influenced by light, heat, dilution, and time of standing, all of which factors promote the formation of a substance which reacts with acid potassium iodide solution as does $HIO_3$ liberating iodine. It is presumed that this substance is $HBrO_3$. Vieböck acknowledges the possible formation of this compound, and suggests that it is brought about by the presence of undissolved sodium acetate in the solution prior to the addition of the formic acid.

Probably he intended to say that its formation was due to too little dissolved sodium acetate.

The errors to which Vieböck's solution gave rise were entirely overcome by using as absorbing solution bromine dissolved in aqueous potassium bromide.
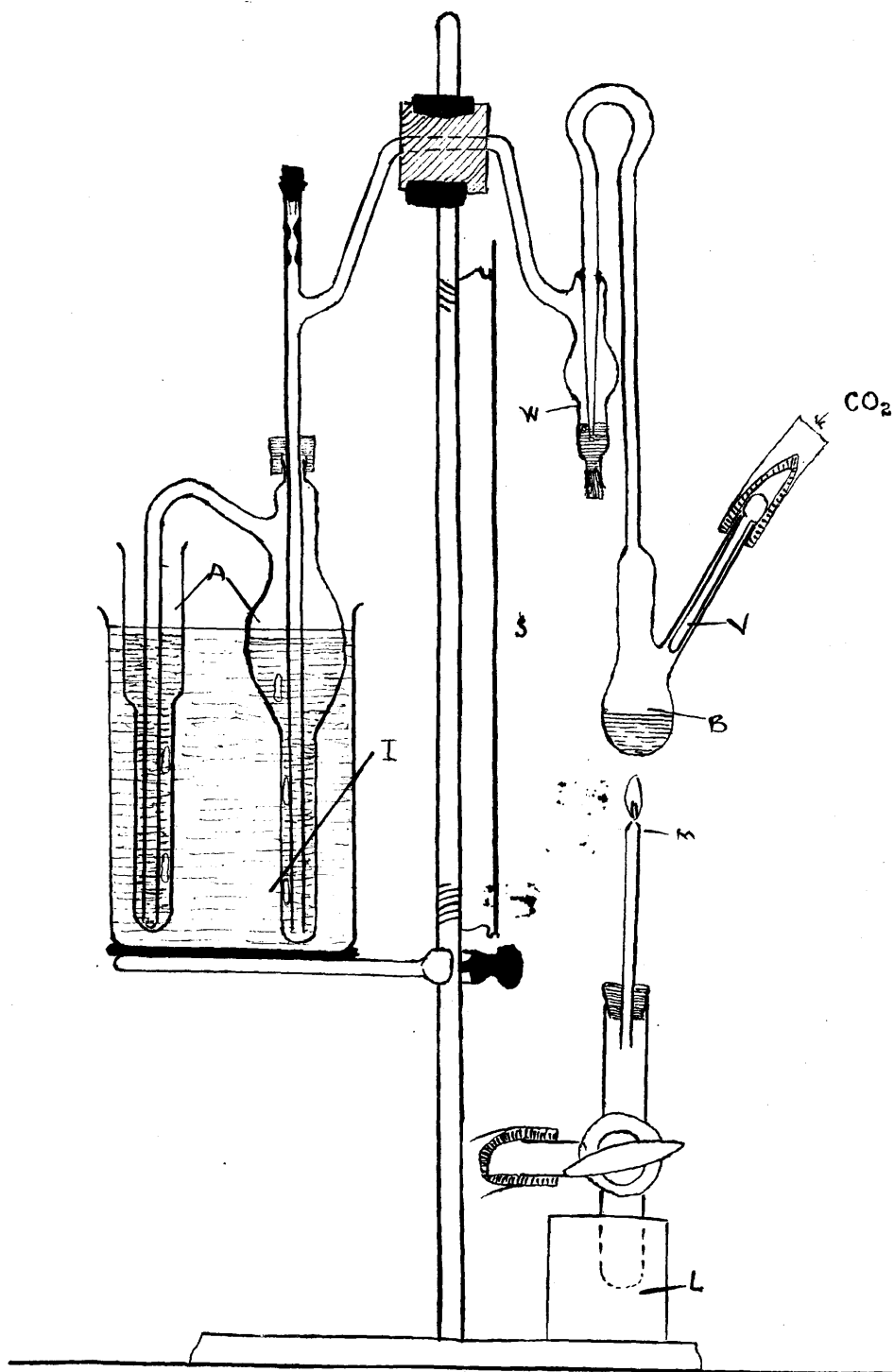
CO₂

L. Lead base.        V. "Verschlusstäbschen."
M. Micro burner.     S. Asbestos shield.

I. Ice water.        A. Absorption tubes.

B. Boiling flask.    W. Washing chamber.

Procedure.

The apparatus (fig. opposite) is after Lieb[26], and with the exception of the absorbing vessels, is made of Jena glass. The absorbing vessels are of ordinary soft glass.

The apparatus, cleaned and thoroughly dried, is erected on a retort stand. About 3 cc. hydriodic acid is pipetted into the boiling flask via the side arm, and a knife edge of phosphorus dropped in to prevent bumping during the boiling of the acid in the flask. Enough washing solution (sodium bicarbonate saturated solution is efficient) put into the washing chamber to just cover the tip of the delivery tube entering from the boiling flask.

The absorbing solution is freshly prepared for each estimation by adding 0.05 cc. bromine to 18 cc. 20% aqueous potassium bromide solution. This solution is made homogeneous and divided into two equal parts.

One of these, contained in a test tube serves as a control and is kept under the same conditions as the absorbing solution proper, the 9 cc. of which are divided so that the first of the absorbing tube receives about 7 cc. and the second the remainder.

The tubes are fitted into position, and the stopper at the top of the vertical delivery tube leading into the absorbing system is moistened and inserted into place.

The "verschlussstäbschen" and $CO_2$ delivery tube are now affixed in position and the stream of gas set gently going.

( The "verschlussstäbschen" should be a neat fit for the side arm, since its function is to prevent splashing by directing the $CO_2$ stream uniformly into the boiling flask.) The flow of $CO_2$ is regulated to allow only two bubbles to be in the absorbing solution at one time.

When the $CO_2$ stream has been regulated the verschlusstäbschen and delivery tube are withdrawn and the tin foil tube containing the weighed out compound slipped into the boiling flask, and the side arm closed again.

Heating is commenced gently, with a micro flame about ¼ cm. of which is visible, and the tip of which is about 1 cm. from the bottom of the boiling flask.

The tin foil tube containing the compound is made by cutting a piece of tin foil about 1 cm. square and rolling this around a piece of thin glass rod.

The weight of compound taken should be 1-5 mg.

Heating is continued for 40 minutes, i.e., about 5 minutes after bumping begins.

Thereafter, the combined absorbing solutions are washed into a flask with 45 cc. of 25% potassium acetate solution and the bromine destroyed by addition of formic acid (1 cc. of 85%). 2 cc. of 10% potassium iodide solution is added and 25 cc. of 5N sulphuric acid added and the liberated iodine titrated with $N/50$ sodium thiosulphate solution.

The control is similarly treated and any titration for this is subtracted from the titration of the absorbing solution.

Generally the control is not more than 0.10 cc. representing 1-3% of the total titration.

During the experiment the control and absorbing vessels are contained in a darkened beaker containing ice water.

After each experiment the hydriodic acid with crust of tin chloride and organic residue is withdrawn from the boiling flask, put into a residue bottle and the contents of this filtered from time to time and the acid used over again.

This was found to be an advantage over the method of doing three or more experiments with one filling of acid.

(4) <u>The Estimation of Carbon and Hydrogen in</u>
<u>Organic Compounds.</u>

(a) <u>The use of a Pt/Rh contact instead of</u>
<u>Pregl's Universal filling.</u>

(b) <u>A new principle for the elimination of</u>
<u>oxides of nitrogen.</u>

The completeness with which the combustion of sulphur, -
and halogen - containing compounds was effected with Pt/Rh
contact suggested that a similar method might be applicable to
the determination of carbon and hydrogen.

The Pregl[3] filling consists of suitably spaced copper
oxide, lead chromate, silver foil, asbestos and lead peroxide.

The lead compounds and the asbestos are hygroscopic and
are the source of discrepancies in the estimation of hydrogen
whilst the lead peroxide suffers the further drawback of removing
oxides of nitrogen only in the comparatively small temperature
range $190^{\circ}$-$220^{\circ}$C.

Below the former temperature it combines with the oxides
of nitrogen too slowly, whilst above $220^{\circ}$C it decomposes and
fouls the combustion tube.

The aim of this work was to overcome the necessity to
use Pregl's Universal filling, and the foremost alterations in
the system were the use of the platinum-rhodium gauze and the
introduction of a constriction at the exit which permitted the
gases to flow at 3 cc./min. thus overcoming the need for an
asbestos constriction.

No difficulties were experienced in the analysis of
substances containing only carbon and hydrogen (and oxygen)
when the Pt/Rh contact was used, and the few substances analysed
(see page 61) were sufficient to give the work a foundation
for the next step, - to try to overcome the production of nitrogen
oxides in the combustion of nitrogen containing substances.

The idea was that in decomposing a compound containing
carbon, hydrogen, oxygen and nitrogen in a limited supply of
oxygen, all the nitrogen is likely to be liberated as elementary
nitrogen. In this way any oxide of nitrogen initially produced
in the decomposition of the compound would be reduced to molecular
nitrogen by the carbon and hydrogen still unoxidised.

This was effected by the preliminary charring of the
compound in a closed tube introduced into the combustion tube
instead of the usual boat. The closed tube was then opened in
situ, and the entering oxygen oxidised and swept out the contents
of the tube.

The dried gaseous products of combustion etc. were passed
into potassium iodide solution, and the liberated iodine indicated
the quantity of nitric acid ($NO_2$) formed in the combustion.

As manipulation improved the amount of liberated iodine
became smaller (as ascertained by titration with standard sodium
thiosulphate solution) until a process was evolved whereby even
picric acid liberated no iodine.

Reverting to the actual gravimetric estimation of carbon dioxide, the table on page 61 of the experimental section illustrates the measure of success in replacing the Pregl Universal filling with Pt/Rh gauze.

Fig. 1.

Constriction in Combustion Tube.

Procedure.

(The combustion tube was of the type used by Pregl,
with the exit constricted as shown in fig.1    on page opposite.
The absorption tubes also were of the Pregl type.   The water
absorbing medium was "Anhydrone," and the carbondioxide medium
"Carbosorb."   A mercury manometer was substituted for the Pregl
bubble counter.   The apparatus was assembled as Pregl's.   The
catalyst    Pt/Rh gauze was heated by a cylindrical electric
furnace to $400^{\circ}-500^{\circ}C$.)

For the estimation of Carbon and Hydrogen in compounds
containing only Carbon, Hydrogen and Oxygen.

The apparatus was assembled as described in Pregl's
Quantitative Organic Microanalysis (3rd Edn. English Translation
page 30 ).   The gas flow set at 3 cc. per minute and the carbon
dioxide tube taken off after sweeping of the combustion tube
was over  wiped according to Pregl and weighed at the 10th
minute.

Five minutes after the carbosorb tube is taken off, the
anhydrone tube is disconnected from the combustion tube and it
is treated as the carbosorb tube and weighed at the 10th minute
after disconnection.  (Pregl takes both off at once, weighs the
carbon dioxide tube at the 10th minute, and the water tube at
the 15th.)

The combustion and weighing of products are carried out
in the manner described by Pregl.

A few compounds were analysed by this method quite successfully, and it was decided to go on to the more exacting study of the destruction of the oxides of nitrogen.

The procedure for analysing nitrogen containing bodies is as follows:-

A 1 cm. diameter soft glass tube is drawn out into capillary tubing, the capillary being about mm. bore and very fragile. This is cut off into lengths of about 5 cm., each length is approximately the same weight. They are sealed at one end.

One of these tubes (A) counterpoised against another is weighed, then a quantity of the nitrogen containing compound introduced into it, as a melting point tube is filled. The tube is again weighed, (about 2-4 mg. weight of substance should be contained therein) then sealed about mid way along its length, and the open end discarded. A piece of hard glass tubing about 4 mm. diameter and 1 mm. thick is sealed at one end, and through the open end is introduced a 2 cm. long coil of copper oxidised superficially (in blow pipe flame). This is allowed to cool slightly. Then the small 2 cm. long sealed tube is notched around the top end with a glass knife, and is dried with a chamois leather and slipped into the tube containing the copper oxide coil with the notched end towards the open end of this outer tube.

About 4 cm. from the sealed end, this tube is drawn out until a fine thread-like capillary is obtained. The open end of the tube is now affixed to the suction pump and the tube evacuated considerably. The capillary is sealed and the open end of the tube broken off.

This constitutes the charge.

By careful shaking, the small inner tube can be made to break without spilling the contents into the outer tube.

The outer "bullet" is now wiped with a chamois leather and introduced into the combustion tube. The Carbon Dioxide tube has previously been weighed, in accordance with the system developed for C and H above. Water is not considered here at present, for the difficulty of keeping the "bullet" tubes thoroughly dry during experimentation always tended to make these results high.

After the insertion of the "bullet", heating with a naked flame is commenced around it and the compound begins to distill out of the small tube into the area of the Copper Oxide. Complete reduction of the oxide is noticed and on intensifying the heating the remainder of the compound, which is in a volatile state now, begins to decompose thoroughly and charring is visible inside the tube. When the tube is practically all red hot, heating is reduced and the bullet allowed to cool. The heating and cooling take less than 10 minutes.

Now, the combustion tube must necessarily be able to stand up to this heating with a naked flame and for that reason a silica tube is used. The combustion tube has also to stand a certain amount of strenuous handling, as will be seen in the next step, which glass could not long survive.

At the entrance to the furnace in the combustion tube is a constriction with a silica plug almost filling the tube.

And when the cooling of the small tube is over, it is pushed hard up against this plug by a silica rod inserted through the stopper (rubber) at the entry end of the combustion tube.

Heating is commenced again just behind the bullet tube, and the silica rod presses the bullet home until the thin capillary like nose of it breaks.*

The bunsen is now applied at the base of the "bullet" and oxidation takes place within the bullet slowly as the oxygen enters.

A process of heating and cooling continues on the bullet for some 10 minutes during which oxygen slowly enters the tube and drives out carbon dioxide, etc. The copper is re-oxidised and may be recovered for future use. The products of combustion are swept into the absorption tubes as before, and the carbosorb tube weighed in the usual manner.

The results for this method of combusting are entered in the experimental section of this work.

---

* The preliminary evacuation of the bullet has prevented premature bursting.

# E X P E R I M E N T A L .

For Combined Halogen-Sulphur Determination.

Ammonium Thiocyanate and Iron Alum. Volhard[9]; Cowie and Gibson[8].

Cowie and Gibson applied Volhard's method to the estimation of small amounts of chloride in solution.

The main difficulty in the operation of the method is the observation of the end point.

Attempts were made to intensify the sharpness of the end point.

1a. By filtration and concentration of filtrate.

To increase the sensitivity of the end point, it was proposed to concentrate the silver ion in the test solution.

The silver chloride was precipitated by slowly adding acidulated silver nitrate solution to the heated chloride solution. A point is reached where the silver chloride precipitate coagulates, and at this point, it has been determined, precipitation is complete. The coagulation point itself is not sensitive enough to act as an indication of total precipitation, but it gives a dependable indication of the approach of this.

The precipitate was filtered off and washed with distilled water, the filtrate thereafter being concentrated, to about 1/3 original volume, say 10 cc., iron alum added, and titration with ammonium thiocyanate proceeded with.

The increase in sensitivity was not sufficient to merit acceptance of the method.

1b. <u>With alum as external indicator, with capillary tube</u>.

In a second attempt to increase the visibility of the end point, the filtration-concentration system above was adopted, and titration with ammonium thiocyanate carried out with iron alum as external indicator. The alum was spotted on a glased porcelain tile, and small drops of test solution were extracted after each drop-wise addition of thiocyanate, by means of a capillary tube and spotted on the indicator. The volume of solution extracted by capillary was about 0.02 cc. The method was not a success as the red iron salt was formed irregularly along a series of spots of alum.

1c. <u>Absorption Layer</u>.

Amyl alcohol and ether were added to the solution containing the excess silver nitrate, and formed a layer on the surface of the water. Iron alum was present in the solution. Ferric thiocyanate and silver thiocyanate may be partially separated from each other by the organic layer which tends to hold the silver thiocyanate, thus leaving the concentrated iron salt to colour the solution. Actually the separation is not very complete, the silver thiocyanate precipitate lingering near the interface of the two layers.

The use of ammonium thiocyanate and iron alum was discontinued because of the indefiniteness of the end point.

1a.     Sodium chloride titrated with acidulated silver nitrate solution to a point in excess of coagulation point. Ammonium thiocyanate titrated the excess silver nitrate, iron alum as internal indicator. Volume of solution = 25 cc. Iron alum used 0.5 cc. 1% solution.

| Sodium Chloride (N.F.0.0101) cc. | AgNO$_3$ (0.0141) cc. | NH$_4$CNS (0.00668) cc. | AgNO$_3$ found cc. | for NaCl reqd. cc. |
|---|---|---|---|---|
| 5 | 3.95 | 1.11 | 3.42 | 3.58 |
| 5 | 3.80 | 0.57 | 3.53 | " |
| 5 | 3.73 | 0.12 | 3.67 | " |
| 5 | 3.69 | 0.14 | 3.62 | " |
| 5 | 3.70 | 0.42 | 3.49 | " |
| 5 | 3.61 | 0.17 | 3.52 | " |
| 5 | 3.75 | 0.37 | 3.57 | " |

1b.     Spots of iron alum solution were placed on a tile and to solution containing 5 cc. sodium chloride 3.75 cc. Silver Nitrate solution was added slowly and with shaking.

From normality of solutions.

5.00 cc. NaCl Soln. = 3.58 cc. AgNO$_3$ Soln.

this gave an excess of AgNO$_3$ Soln. = 0.17 cc.

The ppte. was filtered off and washed with hot acidulated water. The filtrate and washings, about 30-40 cc., were evaporated down to 10 cc., and titrated with ammonium thiocyanate with the following results.

| Spot | | 1. | 2. | 3. | 4. | 5. | 6. | 7. | 8. | 9. | 10. | 11. | 12. | 13. | 14. | 15. | 16. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Iron Alum 0.02 cc. | | | | | | | | | | | | | | | | | |
| NH$_4$CNS titre. | cc. | 0.20 | 0.22 | 0.24 | 0.26 | 0.28 | 0.30 | 0.32 | 0.34 | 0.36 | 0.38 | 0.40 | 0.42 | 0.44 | 0.46 | 0.48 | 0.50 |
| Spot indicates end point? | | No | No | No | Yes | No | No | Yes | Yes | No | Yes | No | No | No | Yes | Yes | Yes |
| Correspond. vol. AgNO$_3$ | | 0.09 | 0.10 | 0.11 | 0.12 | 0.13 | 0.14 | 0.15 | 0.16 | 0.17 | 0.18 | 0.19 | 0.20 | 0.21 | 0.22 | 0.23 | 0.24 |

The solution was well shaken before each test was taken.

1c.     No results were obtained for the absorption layer method since this was an observation of colour intensity in the first case.

2a.  Potassium Chromate.  Mohr[10].

The sodium chloride solution (about 3-5 cc. measured accurately) was diluted to 10 cc. and about 0.5 cc. 1% Potassium Chromate added as indicator.  The results, tabulated below, show high generally.  The end points were visible only with difficulty.

2b.     The use of capillary tube was again resorted to, in order to intensify the sharpness of the end point.  Potassium Chromate was used externally as indicator.  The results did not show any improvement over the ones obtained in the first instance.  The solution was shaken before each capillary spot was extracted.

2a.     Potassium Chromate as internal indicator.

| Sodium Chloride | Silver Nitrate | |
|---|---|---|
| (0.0101) | (0.0127) | |
| | found | required |
| 3.00 cc. | 2.57 cc. | 2.40 cc. |
| 3.50 cc. | 2.98 cc. | 2.80 cc. |
| 3.98 cc. | 3.27 cc. | 3.16 cc. |
| 4.50 cc. | 3.62 cc. | 3.58 cc. |
| 4.74 cc. | 3.81 cc. | 3.77 cc. |
| 5.01 cc. | 4.07 cc. | 3.99 cc. |

3.  Potassium Cyanide.

After precipitating the chloride by addition of silver nitrate solution in excess, the solid matter was filtered off

and washed.  The filtrate was treated with KCN solution.  A precipitate formed and this slowly dissolved on continued addition of Potassium Cyanide.  No point was determined where the last solid particle redissolved, a haziness existing in the solution long after enough KCN had been added to redissolve the $AgNO_3$.

## Silver Iodate.

Berends[12] suggested method for chloride determination depends on the insolubility of silver iodate in 20% alcoholic solution.

In the estimation of chloride in presence of sulphate by this method the silver sulphate is precipitated out of the alcoholic solution also.  In order to overcome this unwanted precipitation, nitric acid may be added.  Unfortunately the nitric acid increases the solubility of the silver iodate.

Method.  (Sodium chloride solution treated with Silver Nitrate solution, the excess nitrate filtered off and treated with potassium iodate).

Silver iodate precipitated, excess potassium iodate filtered off, residue washed with 20% alcoholic solution.  Filtrate and washings treated with potassium iodide and nitric acid and titrated with sodium thiosulphate.

$$NaCl \ + \ AgNO_3 \ \rightarrow \ NaNO_3 \ + \ AgCl$$

$$AgNO_3 \ + \ KIO_3 \ \rightarrow \ KNO_3 \ + \ AgIO_3$$

$$KIO_3 \ + \ HNO_3 \ \rightarrow \ KNO_3 \ + \ HIO_3$$

$$KI \ + \ HNO_3 \ \rightarrow \ KNO_3 \ + \ HI$$

$$HIO_3 \ + \ 5HI \ \rightarrow \ 3H_2O \ + \ 6I$$

$$2I \ + \ Na_2S_2O_3 \ \rightarrow \ Na_2S_4O_6 \ + \ 2NaI$$
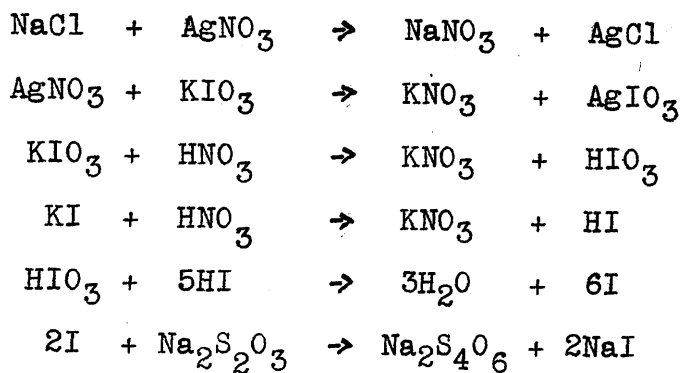
Total vol. soln. = Cl 25 cc.

| Alcohol cc. | $AgNO_3$ (ctg.2.5% $HNO_3$) 0.0100N cc. | $KIO_3$ 0.00995N cc. | $Na_2S_2O_3$ 0.0119N cc. | $AgNO_3$ requires $KIO_3$ cc. | $AgNO_3$ found for $KIO_3$ cc. |
|---|---|---|---|---|---|
| 0 | 1.00 | 1.50 | 0.62 | 1.01 | 0.76 |
| 0 | 1.00 | 1.50 | 0.71 | 1.01 | 0.65 |
| 2 | 1.00 | 1.50 | 0.63 | 1.01 | 0.76 |
| 2 | 1.00 | 2.00 | 1.09 | 1.01 | 0.70 |
| 2 | 1.00 | 2.00 | 1.06 | 1.01 | 0.73 |
| 4 | 1.00 | 2.00 | 1.12 | 1.01 | 0.66 |
| 4 | 1.00 | 2.06 | 1.10 | 1.01 | 0.68 |
| 0 | 2.00 | 2.50 | 0.61 | 1.01 | 0.89 |

## Mercuric Oxycyanide.

Vieböck's[1] method for halogen estimation was applied to the determination of small amounts of chloride.

Conditions of Experimentation.

Solution.    Sulphuric acid standardised against

Sodium Carbonate    Me. Red. Meth. Blue indicator

Normality factor  =  0.00973.

Sodium Chloride solution. N.F.(by weight) 0.00878

Mercuric oxycyanide solution:  Cold saturated
1.30% approximately.

The following table illustrates the change in equilibrium, due to hydrolysis, of the following reaction:-

$$2Hg(OH)(CN) + 2NaCl \rightleftharpoons Hg(CN)_2.HgCl_2 + 2NaOH.$$
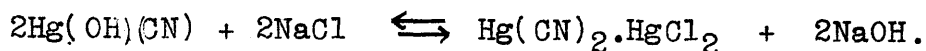
| Sodium Chlor. | Hg(OH)(CN) Sat. soln. | Sulphuric Acid found | Sulphuric Acid required. | Final dilutn. |
|---|---|---|---|---|
| cc. | cc. | cc. | cc. | cc. |
| 2 | 1 | 1.79 | 1.80 | 9.8 |
| 2 | 1 | 1.81 | 1.80 | 12.0 |
| 2 | 1 | 1.79 | 1.80 | 15.0 |
| 2 | 1 | 1.75 | 1.80 | 17.0 |
| 2 | 2 | 1.80 | 1.80 | 10 |
| 2 | 2 | 1.81 | 1.80 | 15 |
| 2 | 2 | 1.80 | 1.80 | 18. |
| 2 | 3 | 1.79 | 1.80 | 15 |
| 2 | 4 | 1.81 | 1.80 | 10 |
| 2 | 10 | 1.80 | 1.80 | 14 |
| 2 | 10 | 1.79 | 1.80 | 14 |
| 3 | 10 | 2.72 | 2.70 | 18 |
| 4 | 10 | 3.62 | 3.60 | 20 |

It will be observed that so long as the concentration of mercuric oxycyanide is maintained at a high level no appreciable hydrolysis takes place.

Hence in order to maintain a high concentration of mercuric oxycyanide, 10 cc. saturated neutral solution was decided upon as the standard volume for each estimation. Also total volumes, after titration were kept between 10-20 cc. in order to have standard condition for titre of unknowns.

In order to investigate the influence of sulphate on the titration the experiments giving the following results were performed:-

With 10 cc. Hg(OH)(CN) Solution:-

| NaCl cc. | $Na_2SO_4$ N/100 cc. | $H_2SO_4$ cc. |
|---|---|---|
| 2 | 2 | 1.81 |
| 2 | 3 | 1.80 |
| 2 | 4 | 1.79 |
| 2 | 5 | 1.81 |
| 2 | 6 | 1.79 |

The results show that sulphate does not affect the chloride titration.

Finally, the sulphuric acid was standardised against Sodium Chloride (with mercuric oxycyanide).

Wt. of Sod. Chlor. = 4.915 mg.

Titration $H_2SO_4$ = 8.64 cc.

NF = 0.00972

Wt. of Sod. Chlor. = 2.510 mg.

Titration $H_2SO_4$ = 4.41 cc.

NF = 0.00974.

Combustion Apparatus.

The figure opposite page 8 illustrates the main differences in the Pregl combustion apparatus for chloride, and the apparatus adopted in this work.

That adopted by Cowie and Gibson was different from the latter only essentially in that, instead of the 50 cc. distilling

flask, they used an additional spiral tube of the "adaptor" type dipping into a conical flask.

Where Pregl and Cowie & Gibson employed a long burner, it was found advantageous, from the point of view of maintaining a constant temperature, to employ a cylindrical electric furnace.

Assuming that no difficulties would appear in the estimation of sulphur, and that any likely obstacles would result from the halogen content of compounds for combustion, the question of converting all of the chlorine to hydrochloric acid was first considered.

A method for determining chloride had been established.

The following work was done in an effort to establish a suitable trapping system.

A Pregl-type combustion tube was used in the experiments. Generally the volume of solution required to trap the products of combustion was in the neighbourhood of 5 cc. $^{N}/100$ Alkali solution with a drop or two of Perhydrol solution added.

In operating the oxygen flow, at 3 cc. per minute, often a seal would form in the beads or in the exit, which was constricted to allow a flow of 3 cc./min. These liquid seals had the effect of stopping forward distillation of the compound into the region of the catalyst, with the result that back distillation towards the oxygen entrance took place. (The method of filling the bead tubes with this solution, was to add to a test tube (which had been treated to extract any external alkali) the

standard alkali solution (5 cc.) and suck this up into the bead section of the tube and retain it there.)

To overcome the tendency to form seals: the exit from the tube was enlarged considerably, but the effect was not pronounced, and it was obvious that the volume of solution was the cause of the trouble, since this forms seals: in the beads section. The amount of active alkali could not be reduced, but the concentration could be altered, and, thereafter the alkali was weighed out in a small platinum boat and transferred in the first cases to a test tube, and dissolved in $\frac{1}{2}$-1 cc. distilled water. A drop or two of Perhydrol was added, and this whole sucked into the bead tube.

The total effect of this was that the combustions were carried on in a smooth even fashion, no seals impeding the flow of gases. The test tube was placed over the mouth of the bead tube.

The results for the compound p-di-chloro benzene were however short of what should have been realised by the acidity of the chlorine, and it was concluded that the trapping system was not efficient enough to give all the oxides of chlorine a chance to be reduced.

Finally the 50 cc. distilling flask was introduced into the apparatus. It was more easily handled than the spiral tube proposed by Cowie and Gibson. The side arm of the flask was at first dipped into a small test tube containing alkali (standard solution) with Perhydrol. The trapping system was now quite

satisfactory. The flow of gases broke through the alkali solution in the test tube intermittently. No seals resulted, for the exit from the side arm was wide enough to prevent this.

As a final modification of the apparatus, the side arm of the distilling flask was bent bow shaped and in the centre of its length a small bulb was blown; this bulb acted as a reservoir for the standard alkali solution. It was broken intermittently by the flow of gases and the side arm could be so tilted that the individual bubbles of gas were held in solution for a short time allowing intimate contact of the gases with solution and permitting reduction of the oxides of chlorine.

### Combusting p-dichlorobenzene.

Weight of compound 2-4 mg.

| % Chlorine in Compound | | Remarks. |
|---|---|---|
| Found | Required. | |
| 47.3 | 48.3 | ( 5 cc. Standard alk. used with 2 drops Perhydrol. Liquid formed seals in bead tube. |
| 47.5 | " | ( Solid alkali in 0.5 cc. water with 2 drops Perhydrol.   Smooth flow of gases. |
| 48.4 | " | ( Solid alkali in 0.5 cc. water + Perhydrol |
| 48.0 | " | ( $\frac{1}{2}$ cc. Standard alkali in test tube + Perhydrol with distilling flask side arm dipped therein. |
| 47.9 | " | ( As above but with side arm bent as described. |
| 48.3 | " | |

<u>Compounds Analysed.</u>

| Compounds Analysed. | Sulphur found Per Cent. | Sulphur required Per Cent. | Chlorine found Per Cent. | Chlorine required Per Cent. | Bromine found Per Cent. | Bromine required Per Cent. |
|---|---|---|---|---|---|---|
| Dichlorobenzene $C_6H_4Cl_2$ | - | - | 48.3  48.4 | 48.3 | | |
| Tetrachloro diphenyl disulphoxide $C_{12}H_6O_2S_2Cl_4$ | 16.5 | 16.5 | 36.7 | 36.5 | | |
| Chlorophenylsulphonacetone $C_6H_9O_3SCl$ | 13.6 | 13.5 | 15.3 | 15.1 | | |
| Ethyl Chlorocamphorsulphonate $C_{12}H_{18}O_3SCl$ | 11.4 | 11.5 | 12.5 | 12.1 | | |
| Dichlorophenylsulphone $C_{12}H_{18}O_2SCl_2$ | 11.1 | 11.3 | 25.2 | 25.1 | | |
| Tetrachloro diphenyl disulphide $C_{12}H_6S_2Cl_4$ | 17.7 | 17.9 | 39.4 | 39.9 | | |
| Naphthalene sulphonchloride $C_{10}H_7O_2SCl$ | 14.0 | 14.2 | 15.8 | 15.7 | | |
| Toluenesulphonchloride $C_7H_7O_2SCl$ | 16.4 | 16.8 | 18.5 | 18.1 | | |
| Ethyl Bromocamphorsulphonate $C_{12}H_{18}O_3SBr$ | 9.69 | 9.94 | | | 24.6 | 24.8 |
| Bromo Phenylmethylsulphone $C_7H_7O_2SBr$ | 13.9 | 13.6 | | | 34.0 | 34.0 |
| $CH_3OC(CH_3)_2SO_2C(SO_2Me)Br_2$ | 16.2 | 16.5 | | | 40.8 | 41.2 |
| (cyclic structure below) | 24.0 | 24.4 | | | 29.9 | 30.4 |
| Tolyldibromopropylsulphone $C_{10}H_{12}O_2SBr_2$ | 9.28 | 9.00 | | | 45.8 | 45.0 |

Structure for the row with values 24.0 / 24.4 / 29.9 / 30.4:

```
CH2 ——— SO2
 |         \
CH2 ——— SO2  C — CH3
              |   \
             Br    CH3
```

For Sulphur in presence of Nitrogen and Halogen.

### Rhodizonic acid. (Strebinger and von Zombory[16])

The barium salt of rhodizonic acid is red in colour, the sodium yellow in dilute solution. Hence, in neutral sulphate solution, the formation of the barium salt is taken as the end point in the titration of sulphate with a standard barium solution. The change at the end point is from the yellow of the sodium salt to the red of the barium.

In any of the experiments done with the indicator used internally no definite yellow-red change was observed. Attempts were made to use the solution of the sodium salt as external indicator with the following results:-

A series of spots were placed on different substances, Porcelain tile, Silica tile, Filter paper and washed linen. The undernoted table gives the results obtained.

Normality factor Sulphate solution  =  0.00963

    "        "     Barium     "     =  0.00844

The solutions were accurately made up with pure reagents in distilled water.

1 cc. Sulphate should require 1.14 cc. Barium solution.

### Experiment.

2 cc. $Na_2SO_4$ solution titrated into beaker, diluted to 15 cc. and titrated with Barium Nitrate solution slowly. After each addition of Barium solution, a test spot was conveyed by

capillary tube to the rhodizonate spot.  The following results were obtained.

| Spot | 1 cc. | 2 cc. | 3 cc. | 4 cc. | 5 cc. | 6 cc. | 7 cc. | 8 cc. | 9 cc. | 10 cc. | 11 cc. | 12 cc. | 13 cc. | 14 cc. | 15 cc. | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| On Porcelain | 1.81 | 1.87 | 1.90 | 1.94 | 2.01 | 2.07 | 2.13 | 2.18 | 2.24 | 2.29 | 2.33 | 2.45 | 2.50 | 2.55 | 2.70 | Ba(NO3)2 |

Red Barium Rhodizonate developed at -
1.94, 2.01, 2.07, 2.24, 2.45, 2.50, etc. cc.

| On Filter (A) | 1.80 | 1.86 | 1.91 | 1.96 | 2.01 | 2.06 | 2.10 | 2.14 | 2.18 | 2.23 | 2.28 | 2.33 | | cc. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Paper (B) | 1.89 | 1.94 | 1.98 | 2.02 | 2.07 | 2.12 | 2.16 | 2.22 | 2.27 | 2.31 | 2.36 | 2.42 | 2.45 | cc. |

(A) Spots developed at 2.14, 2.28, 3.33 cc.

(B) Spot developed only at 2.31 cc.

| On Linen | 1.85 | 1.87 | 1.92 | 2.01 | 2.05 | 2.10 | 2.15 | 2.19 | 2.24 | 2.28 | 2.33 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| On Silica | 1.83 | 1.87 | 1.92 | 2.01 | 2.05 | 2.10 | 2.15 | 2.19 | 2.24 | 2.28 | 2.33 |

On Linen - Spots developed only at 2.10, 2.15 cc.

On Silica - Spot developed only at 2.33 cc.

Since the forward titration method was not practicable using sodium rhodizonate as external indicator, a back titration method was tried out. The excess Barium was treated with sulphate and spots were taken out of the solution by capillary tubes (a fresh tube for each spot) in the hope that the red barium colour would sharply disappear. This method was no more successful than the former.

Tetrahydroxy quinone.

This substance proposed by Schroeder[17] as an indicator for Barium was no more successful in application than Rhodizonic acid. The two compounds are used in precisely the same way with the same colour changes.

The tetrahydroxy quinone (sodium salt) was tried out as an external indicator in the manner above.

| No. of Test | Conditions of Experiment. | Vol. Sulphate used. cc. | Pink Spot first developed at cc. | $\dfrac{Ba^{++}}{SO_4{}''}$ |
|---|---|---|---|---|
| 1. | Spot on Porous Plate | 2.00 | 2.34 | 1.17 cc. |
| 2. | " " " " | 2.18 | 2.65 | 1.21 cc. |
| 3. | " " " " | 3.00 | 3.38 | 1.13 cc. |
| 4. | " " Filter Paper | 2.50 | 3.15 | 1.26 cc. |
| 5. | " " " " | 2.00 | 2.18 | 1.09 cc. |
| 6. | With HCl added no Pinking developed. | | | |
| 7. | Spot on Cloth (Linen) | 2.00 | 2.10 | 1.05 cc. |
| 8. | " " Silica | 2.00 | 2.33 | 1.17 cc. |
| 9. | " " " | 2.00 | 2.08 | 1.04 cc. |

## Benzidine Sulphate (Drummond[19])

The solubility of Benzidene sulphate is about 0.05 gms. per litre, and is said to be considerably less in mixtures of water and acetone.

Benzidene Sulphate in dilute solution is hydrolysed into a weak base and strong acid. The acid, sulphuric, may be estimated with alkali solution.

Applied to micro analysis, the method was of no avail, the solubility of the sulphate being too great for accurate results to be obtained, even in 80% acetone solution.

## Stability of Potassium Bisulphate. (Friedrich[2].)

Friedrich evolved a method for sulphate estimation based on the stability of Potassium Bisulphate.

The system was to add to a sulphuric acid solution neutralised exactly, a volume of sulphuric acid equivalent to the alkali for neutralisation. Bisulphate was thus formed. Careful evaporation to dryness followed and the salt redissolved and titrated, always giving evidence that the Bisulphate was quite stable after continual heating. This was of particular value where other more volatile acids were in solution as these were evolved.

In the present consideration it was discovered that a large excess of Sodium Sulphate could be present in solution of Sodium bisulphate (and Nitric) and the bisulphate would still remain stable.

| $HNO_3(0.0170)$ | $H_2SO_4(0.00912)$ | $Na_2SO_4(0.0210)$ | Alk.found (0.0113) | Alk.reqd. |
|---|---|---|---|---|
| 1 | 3 | 5 | 2.49 | 2.48 |
| 3 | 3 | 5 | 2.50 | " |
| 1 | 3 | 6 | " | " |
| 3 | 3 | 6 | " | " |
| 2 | 3 | 8 | " | " |
| 5 | 3 | 6 | " | " |
| - | 3 | 10 | " | " |

When Friedrich's method was applied to products of combustion of a sulphur   containing compound , the following results were obtained.  Propylenediphenylsulphone.

| Sulphur direct titration | Sulphur (after Friedrich) | | Sulphur required |
|---|---|---|---|
| 19.6% | 18.6% | 18.4% | 19.8% |
|  | 17.9% | 17.0% |  |

As the discrepancy was probably due to incomplete conversion of $SO_2 \rightarrow SO_3$ by the perhydrol, chlorine water was substituted.

Here the results were variable, high ones as the result of retention of hydrochloric acid (as indicated by Silver Nitrate) causing the rejection of the method.

| Compounds. | Sulphur found Per Cent. | Sulphur required Per Cent. |
|---|---|---|
| Propylenediphenylsulphone | 19.7 | 19.8 |
| Toluenesulphonamide | 18.6 | 18.7 |
| Thiourea | 42.3 | 42.1 |
| Dinitrophenyl disulphide | 20.0 | 20.8 |
| 4-Chloro-3-nitro,4'-2' dinitro-diphenylsulphone | 6.25 | 8.21 |
| Nitrodiphenyl sulphide | 15.7 | 13.8 |
|  | 13.4 |  |

The evaporations were done in a silica distilling flask 200 cc. capacity, with a silica tube inserted and held in place just over the solution. The outer end of the tube was affixed to suction apparatus and a gentle stream of filtered air drawn through the system to help the evaporation of the solution in the flask which was immersed in boiling water in a water bath.

## Barium Chromate Precipitation.

A weighed out quantity of $BaCl_2.2H_2O$ was dissolved in water. A large excess of Potassium Chromate added slowly and yellow Barium Chromate was precipitated. The excess K chromate was filtered off. The precipitate washed with 50% Alcohol and the Hydrochloric acid and a crystal of Potassium iodide added. The liberated iodine was titrated with sodium thiosulphate (and using starch as indicator).

|     | $BaCl_2.2H_2O$ | Thiosulphate |
|-----|----------------|--------------|
| (1) | 0.998 mg.      | 0.99 cc.     |
| (2) | 1.319 "        | 1.31 cc.     |

(1)  $BaCl_2.2H_2O$ in 20 cc. water.
(2)  $BaCl_2.2H_2O$ in 30 cc. water.

The concurrency of the results suggested that the method might be practicable, and this was so.

The apparatus for combusting was the same as for Chlorine and Sulphur determination. The procedure in the initial stages was the same. It was necessary to introduce a small pre catalyst

at the entrance to the furnace area, in order to promote dis-
ruption of some of the more stable compounds. This was heated
to between $500^{\circ}$-$600^{\circ}$C.

After washing the tube, the total acidity was ascertained
and this gave the utmost volume of Barium Chloride solution to
be added for precipitation of Sulphate.

The solutions used were $N$/100 Barium Chloride and Sodium
Thiosulphate, strong solution of Potassium Chromate and solid
Potassium Iodide.

## Compounds Analysed.

| Compounds Analysed. | Sulphur | |
|---|---|---|
| | found Per Cent. | required Per Cent. |
| Propylenediphenylsulphone $C_{15}H_{16}O_4S_2$ | 19.5 | 19.8 |
| Camphor sulphonylmethylsulphonylmethane $C_{12}H_{20}O_4S_2$ | 21.2 | 20.8 |
| Benzyl sulphonylmethylsulphonylmethane $C_9H_{12}O_4S_2$ | 25.7 | 25.9 |
| Thiourea $CH_4SN_2$ | 42.8 | 42.1 |
| " | 42.3 | - |
| Dinitrodiphenyl disulphide $C_{12}H_9O_2SN$ | 13.8 | 13.8 |
| Toluenesulphonamide $C_7H_9O_2SN$ | 18.4 | 18.7 |
| Cystine $C_6H_{12}O_4S_2N_2$ | 26.6 | 26.7 |
| Nitrodiphenyl sulphide $C_{12}H_9O_2SN$ | 13.8 | 13.8 |
| Sulphanilic acid $C_6H_7O_3SN$ | 18.5 | 18.5 |
| Thiocarbanilide $C_{13}H_{12}SN_2$ | 14.1 | 13.9 |
| Phenyl-sulphonyl-acetonitrile $C_8H_7O_2SN$ | 17.4 | 17.7 |
| " | 17.5 | |
| 4-Chloro-3-nitro, 2'-nitro-4'-nitro-diphenylsulphone $C_{12}H_6O_8SN_3Cl$ | 8.25 | 8.25 |
| 4-Bromo-3-nitro, 2'-nitro-4'-nitro-diphenylsulphone $C_{12}H_6O_8SN_3Br$ | 7.27 | 7.41 |
| 4-Chloro-2'-nitro-4'-nitro-diphenylsulphone $C_{12}H_7O_6SN_2Cl$ | 9.11 | 9.37 |

3.  **Hydriodic acid**.                    **Repeating Vieböck and Brecher**.

The hydriodic acid which was first used was by no means fresh and on results being obtained for Vanillin which were high and always irregular.  It was presumed that the hydriodic acid and the washing solution were not efficient, the former evolving hydrogen iodide, and the latter, which was sodium thiosulphate not being able to cope with this evolution, was allowing it through and into the absorbing solution.

The hydriodic acid was investigated itself.  A blank was run and the Bromine solution gave a titration which seemed to prove that the hydriodic acid was at fault.  A fresh supply was obtained, but still the blanks gave a titration.

The flame was reduced in heating power and the length of time of heating altered, varying from 20-40 minutes.  Still the Bromine Solution of Vieböck  gave a precipitate of iodine when treated in accordance with his system.

The hydriodic acid (1. 7   ) was beyond reproach.  To control heating Vieböck's glycerol bath method was tried out.

This definitely was a drawback to the experimentation since if it acquired a temperature, and it was necessary to lower this quickly, the free flame on the boiling tube was the better method of heating.

Investigation of the washing solution was now commenced, and a variety of substances tried.

Blanks were run on hydriodic acid with the following substances as washing agents.

Potassium iodide[27] crystals, moistened with water and packed into the washing chamber. The tinge of yellow iodine on KI was visible on these crystals after boiling of the blank had proceeded for about 25 minutes though the lack of intensity of this stain suggested that only a very small quantity of iodine was being evolved.

Nevertheless, the absorbing solution showed evidence, when treated, of iodine precipitated and accordingly the moist KI crystals gave way to saturated KI solution.

This proved no better, and a series of mixtures were tried out:- $CaCO_3$ paste with KI. Sodium Thiosulphate solution and saturated sodium bicarbonate solution.

All were apparent failures, and it was only by the fortuitous blocking up of the entrance into the washing chamber by the $CaCO_3$ paste that the investigation of the washing solution was ceased and interest turned to the absorbing solution.

## Investigation of Viebock's solution.

Solution made up as described, 10 cc. of this taken and 2 drops bromine added.

A group of 7 tests were made on solutions of the same composition. At the end of various periods of time the test was treated with 10 cc. Sod. acetate ($\frac{1}{2}$-1 gm. Solid Solution 1 cc. of 50% formic acid, 2.5 cc. 10% KI solution, and 1 cc. $H_2SO_4$ Iodine starch added and the solution titrated to an end point with Thiosulphate. All tests kept at room temperature in conical flasks.

| Time of Standing | Thiosulphate Titration. |
|:---:|:---:|
| min. | cc. |
| 10 | 0.15 |
| 15 | 0.18 |
| 20 | 0.47 |
| 25 | 0.24 |
| 30 | 0.32 |
| 35 | 0.84 |
| 60 | 0.85 |

Conclusion:-   That solution cannot be successfully used in accurate determinations.


Viebӧck's Solution continued.

All tests and operations carried out in ice cooled vessels.   Ten tests treated as above, and having same composition.

| Time of Standing. | Titration Thiosulphate. |
|:---:|:---:|
| min. | cc. |
| 10 | 0.16 |
| 20 | 0.17 |
| 25 | 0.12 |
| 30 | 0.13 |
| 35 | 0.13 |
| 40 | 0.18 |
| 45 | 0.13 |
| 100 | 0.40 |
| 105 | 0.46 |
| 110 | 0.39 |

Irregularity suggested that method could not be applied to accurate analysis.  Ice cooling had effect of slightly reducing auto-formation of oxidising substance stable to formic acid.

Viebőck's Solution Continued.

As before. (In ice.)

Adding after lapse of time

$\frac{1}{2}$-1 mg. dissolved Sod. Acetate, 1 cc. Formic 50%

2.5 ml. 10% KI + <u>2</u> cc. $H_2SO_4$ → Iodine. S/Thios.

| Time of Standing. | Titre. |
|---|---|
| min. | cc. |
| 5 | 0.61 |
| 10 | 0.69 |
| 15 | 0.69 |
| 20 | 0.77 |
| 30 | 0.79 |
| 35 | 0.80 |

And with solutions for 20,30 and 40 minutes duplicates were
run with increase in $H_2SO_4$ added, thus:-

|  | 2 cc. $H_2SO_4$ | 2.5 cc. | 4 cc. |
|---|---|---|---|
| 20 mins. | 0.77 | 0.98 | - |
| 30 mins. | 0.79 | 1.10 | - |
| 40 mins. | 0.80 | - | 1.65 |

Suggesting that Iodine was precipitated according to the amount
of $H_2SO_4$ present and also to length of time of standing, the
second factor depending on the first in so far as the precipita-
tion of Iodine was comparatively slow.

Bromine in Potassium Bromide.

Solution 2 drops in 10 cc. of 10% KBr solution.

| Sodium acetate | 15% solution |
|---|---|
| Formic acid | 50% solution |
| Pot. iodide | 10% solution |

Test solutions were treated as before (10 cc. Na $\bar{A}$. + 1 cc.H.COOH
(Br$_2$ in KBr) (+ KI + H$_2$SO$_4$)

| Time of Standing | Titre. |
|---|---|
| mins. | cc. |
| 5 | 0.28 |
| 10 | 0.28 |
| 15 | 0.28 |
| 20 | 0.28 |
| 25 (3 cc.H$_2$SO$_4$) | 0.32 |
| 30 (4 cc.H$_2$SO$_4$) | 0.37 |

Conclusion.    Br/KBr Solution does not form HBrO$_3$ and does not

give rise to Iodine precipitating agent in point

of time, but in point of acid concentration.

At this stage the method did not appear hopeful.

Returning to Viebõck's Solution.

Solution made up as before, and 10 cc. measured out

into 10 flasks.

5 of these formed series A and were ice cooled with a

stream of CO$_2$ passing through at 2 bubbles in solution at one

time. The other five, series B, were ice cooled (just).

| Samples. | | Time. | Titres. | |
|---|---|---|---|---|
| A. | B. | min. | A. cc. | B. cc. |
| (1) | | 10 | 0.13 | 0.21 |
| (2) | | 30 | 0.22 | 0.30 |
| (3) | | 35 | 0.20 | 0.20 |
| (4) | | 40 | 0.35 | 0.44 |
| (5) | | 80 | 0.26 | 0.33 |

These suggested that the blank was not dependable as a gauge of

titre from extraneous matter in the experiment proper.

As the Bromine itself might have been the cause of the growth of the "unknown", bromine was prepared from Analar Potassium Bromide.

Acetic acid/K acetate solution. 2 drops Bromine per 10 ml. solution. Ice cooled and solution treated at 10 etc. minutes.

| Time of Standing. | Titre. |
|---|---|
| mins. | cc. |
| 10 | 0.72 |
| 15 | 0.38 |
| 20 | 0.70 |
| 25 | 0.42 |
| 30 | 0.75 |
| 35 | 0.25 |

Showing that the Bromine formerly used must have been pure enough.

## Action of Light on Bromine Solution.

Two similar samples of 10 cc. made up

(a) Sunlight sample
(b) Darkened    "

Samples ice cooled.

| | Titre after 20 mins. | Titre after 40 mins. |
|---|---|---|
| a. | 0.24 | 0.57 |
| b. | 0.15 | 0.22 |

Light encourages formation of $HBrO_3$.

Total darkness however does not prevent it.

Ammonia and Urea were both added to the solution in place of formic acid to reduce the HBrO to HBr.

Solution treated with ammonia and boiled for 5 minutes

Samples had titres up to 4.96 cc. which was out of the question.
Urea titres from 0.08-1.76.

Using 96% acetic acid aqueous solution containing 10 gm.
K acetic 10 cc. + 2 drops Bromine.

| | | |
|---|---|---|
| After 15 mins. | 0.06 cc. | Ice cooled temp. |
| " 15 " | 0.10 cc. | Room temp. |
| " " " | 0.83 cc. | 35% |

Using 100% HA. 10 gms. KA per 100 cc.

10 cc. + 2 dps. Bromine

| | | |
|---|---|---|
| 15 mins. | 0.13 cc. | Room Temperature |
| 20 " | 0.12 " | " " |

## Bromine in KBr.

10% KBr.     10% KA.     10% KI.     H.COOH.

Samples  10 cc. KBr.Soln.   3 drops $Br_2$. ice cooled  pour into
         10 cc. KA Soln.    add 5 cc.HA.  1 cc. Formic acid &
         1 cc. $H_2SO_4$.

| | Min. | Titre. |
|---|---|---|
| 1 | 10 | 0.37 |
| 2 | 15 | 0.37 |
| 3 | 20 | 0.38 |
| 4 | 25 | 0.37 |

Formic acid.

| | | |
|---|---|---|
| 1a | 1.00 | 0.39 |
| 2a | 2.00 | 0.40 |
| 3a | 3.00 | 0.40 |
| 4a | 1.00 | 0.38 |

(Four drops bromine 0.52)

One drop  titre = 0.13 cc.

One drop of Bromine was used, slightly smaller than above. The general value for the titration was less than 0.10 cc. $^{N}/100$ Sod. Thiosulphate Solution.

## Meth. Iodide in Acetic Acid.

1 cc. Solution containing 1.07 mg. M.I.

| MeI. in A.A. | KBr/Br$_2$ | K acetate | Formic | KI | H$_2$SO$_4$ | Titre |
|---|---|---|---|---|---|---|
| 1 cc. | 10cc/3 dps. | 10 | 2 | 1 | 1 | 2.43 |
| " | " | " | " | " | " | 2.45 |
| 2 cc. | " | 20 | " | " | " | 4.86 |
| 3 cc. | " | 30 | " | " | " | 7.36 |
| 4 cc. | " | 40 | Iodine colour revived. | | | |

At the completion of the absorption of the MeI. there is in the A.S. HIO$_3$ HBr HBrO & KBr.

It is necessary to add NaA to cover all of these substances and convert the acids into their salts. The addition of H.COOH caused reduction of the NaBrO to NaBr.

Thereafter for the titration of the iodine enough H$_2$SO$_4$ must be added to cover all the salts for the reason that NaA will be attacked first; KBr next, etc.

Hence a large excess of Na ā is required in the first case and a large excess H$_2$SO$_4$ in the second.

Compounds Analysed.

| Substance | Wt. mg. | OMe,% Found | Reqd. | Substance | Wt. mg. | OMe,% Found | Reqd. |
|---|---|---|---|---|---|---|---|
| Vanillin | 0.544 | 20.5 | 20.4 | p-Methylbenzaldoxime | 2.349 | 20.2 | 20.5 |
| | 0.822 | 20.2 | - | | 2.845 | 20.6 | - |
| | 1.318 | 20.2 | - | Papaverinol | 3.845 | 34.6 | 34.9 |
| | 2.017 | 20.3 | - | p-Methoxybenzilidene-acetophenone. | 3.294 | 12.9 | 13.0 |
| | 2.498 | 20.4 | - | Dibenzoyl p-toluene-sulphonyl methyl glucide. | 4.241 | 5.61 | 5.57 |
| | 3.100 | 20.4 | - | | 3.849 | 5.61 | - |
| | 3.216 | 20.3 | - | Iododibenzoyl p-toluene-sulphonyl methyl-glucide. | 4.610 | 5.02 | 4.55 |
| | 3.592 | 20.2 | - | | 4.613 | 5.02 | - |
| | 4.198 | 20.2 | - | Tetramethyl α-methyl-glucoside. | 1.741 | 60.9 | 62.0 |
| | 4.693 | 20.1 | - | | | | |
| α-Methyl-glucoside | 3.472 | 16.2 | 16.0 | | | | |
| | 3.771 | 16.1 | - | | | | |
| | 3.890 | 16.1 | - | | | | |

## 4. For Nitrogen Peroxide Destruction.

In the investigation of methods whereby the oxides of nitrogen normally formed during the combustion of a nitrogen-containing compound, could be prevented from affecting the carbon determination in such compound, the principle aimed at was one in which reduction of the nitrogen oxides would take place or alternatively oxidation of nitrogen could be prevented.

Molecular nitrogen does not readily combine with oxygen, and it was presumed that once the nitrogen was in this stable state, conditions within the combustion tube were such that union would be negligible.

Experimenting first with Pot. Iodide Solution.

Apparatus lay out:

Combustion tube -"Anhydrone" tube - delivery tube passing into concentrated potassium iodide solution.

## Procedure.

The substance was weighed into platinum boat and this introduced into the combustion tube.

The combustion was carried out as for carbon and hydrogen and the Anhydrone tube trapped the water. The $CO_2$ and $NO_2$ passed on into the Pot. Iodide Solution. Here precipitation of Iodine took place and by titrating the solution after the combustion was finished, it was possible to estimate the iodine precipitated, and hence the $NO_2$ passing into this solution.

## Titration with Thiosulphate/starch.

By this means it was possible to follow the progress being made towards obtaining all of the nitrogen over as molecular nitrogen.

The following table :-

| Compound. | Titration $Na_2S_2O_3$ Solution 1 c.c. = 0.12 mg. $N_2$ | Percent Total $N_2$ | Remarks on System, etc. |
|---|---|---|---|
| Nitrobenzaldehyde | | | |
| 2.796 mg. | 1.06 c.c.    0.13 mg. | 50.2 | Combustion without any application to destruction of $NO_2$. |
| 2.717 mg. | 0.71 c.c.    0.09 mg. | 35.7 | Silver Foil. Wad of Ag foil between Pr boat and gauze, to unite with or reduce $NO_2$. |

| Compound | Titration Na$_2$S$_2$O$_3$ Soln. 1 c.c. = 0.12 mg.N$_2$ | | Percentage Total N$_2$ | Remarks on System, etc. |
|---|---|---|---|---|
| Nitrobenzaldehyde 2.466 mg. | 0.31 c.c. | 0.04 mg. | 17.5 | Ceric oxide. Powdered, inserted at end of tube near outlet. This tended to block tube, and |
| 2.749 mg. | 0.30 c.c. | 0.04 mg. | 15.7 | Ceric oxide with asbestos wool teased through it was tried. This was only slightly more efficient. |
| 2.665 mg. | 0.09 c.c. | 0.01 mg. | 4.0 | Chrysean (as absorbent for NO$_2$) forms dark red ppte. with acid |
| 2.726 mg. | 0.19 c.c. | 0.023 mg. | 9.1 | nitrate. Not effective enough and in any case does not absorb nitrate. |
| 2.546 mg. | 1.01 c.c. | 0.121 mg. | 51.3 | Silver wool, used as a wad at the exit end of the tube. |
| 2.646 mg. | 0.08 c.c. | 0.009 mg. | 3.7 | Copper oxide gauze in combustion tube. Objection to this is that the comb. tubes are readily dis-integrated. |
| 2.637 mg. | 0.10 c.c. | 0.012 mg. | 4.9 | Cold Copper oxide (vide Webb). Length of tube about 8" packed with CuO powder and granules. This tube may have held up some of the NO$_2$ mechanically. |
| 2.418 mg. | 0.14 c.c. | 0.017 mg. | 8.3 | Cu/Ni (as reducing agent in comb. tube) heated. Not effective. |
| 2.761 mg. | 0.26 c.c. | 0.031 mg. | 12.1 | Salicylic acid as absorbed for NO$_2$. Not effective. |
| 2.842 mg. | 0.02 c.c. | 0.003 mg. | 1.1 | Pot. Iodide. Sod. Thios. Anhydrone mixture in tube between Anhydrone tube and K.I. solution. |
| 2.753 mg. | 0.01 c.c. | 0.001 mg. | 0.4 | As above except that starch is |
| 2.773 mg. | 0.08 c.c. | 0.009 mg. | 3.5 | used in place of Na$_2$S$_2$O$_3$. |
| 2.725 mg. | 0.05 c.c. | 0.006 mg. | 2.5 | New filling of K.I. required.for |
| 2.782 mg. | 0.07 c.c. | 0.008 mg. | 3.1 | each pair of experiments. |
| 2.691 mg. | – | – | – | Pot. bisulphate absorbing NO$_2$ (Blank run showed that SO$_2$ was evolved (decolorised KMnO$_4$ Soln. acidified.) |
| 2.863 mg. | 0.15 c.c. | 0.018 mg. | 6.5 | Intermediate tube containing finely powdered Potassium iodide only. This SO$_2$ would react with iodine as it was |
| 2.547 mg. | trace | – | – | Heated in sealed tube Fig. 1 |
| 2.756 mg. | trace | – | – | "   "   "   " with Cu wire. |

| Compound | Titration Na$_2$S$_2$O$_3$ Soln. 1 c.c. = 0.12 mg.N$_2$ | | Percentage Total N$_2$ | Remarks on System, etc. |
|---|---|---|---|---|
| Nitrobenzaldehyde | | | | |
| 2.632 mg. | trace | – | – | No catalyst was used in the combustion tube, otherwise as above |
| 2.888 mg. | – | – | – | |
| 1.907 mg. | – | – | – | Cu Powder (See Note 1 on procedure). |
| 2.617 mg. | – | – | – | The substance was introduced into a small tube about 3 mm. bore, and 2 cm. long having a |
| Picric Acid | | | | |
| 1.872 mg. | 0.01 cc. | 0.001 mg. | – | tail piece about 2 cm.long and |
| 2.857 mg. | 0.01 cc. | 0.001 mg. | – | weighed, then a quantity of |
| 2.216 mg. | 0.01 cc. | 0.001 mg. | – | compound tipped out of this tube into a small hard glass |
| Naphthylamine | | | | tube 3 cm.long, 3 mm. bore. |
| 2.500 mg. | 0.04 cc. | 0.004 mg. | 1.7 | The weighing tube was dried and reweighed for weight of compound |
| 1.914 mg. | – | – | – | used. (C/Nitrogen Micro Dumas). The hard glass tube was evacuat- |
| 1.876 mg. | trace | – | – | ed and sealed, introduced into comb. tube and the compound de- |
| 2.107 mg. | trace | – | – | composed by heating. Cu powder was there as reducing agent, but it was more probable that the absence of NO$_2$ in the K.I. Soln. was due redn. by Carbon and Hydrogen. |

Experience in the above combustions showed that the small hard glass tubes were difficult to break, and on account of their shortness, volatilisation of the compound under pressure was a possibility. Hence the shape of the tube and procedure were altered to suit circumstances and upon analysis of Nitrobenzaldehyde by the procedure described on page 25 the following results were obtained, and are here presented without claim being made that the analysis for carbon in compounds containing nitrogen will always be as successful:-

| | Nitrobenzaldehyde. Weight. | Per Cent Carbon = 55.6 Weight of Carbon Dioxide. | Per Cent Carbon. |
|---|---|---|---|
| 1. | 1.903 mg. | 3.844 mg. | 55.1 |
| 2. | 1.625 mg. | 3.345 mg. | 55.2 |
| 3. | 2.357 mg. | 4.753 mg. | 55.1 |
| 4. | 2.344 mg. | 4.716 mg. | 55.0 |
| 5. | 2.423 mg. | 4.684 mg. | 52.7 × |
| 6. | 2.478 mg. | 4.904 mg. | 54.0 × |
| 7. | 2.330 mg. | 4.710 mg. | 55.0 |
| 8. | 2.305 mg. | 4.421 mg. | 52.3 × |
| 9. | 2.024 mg. | 4.027 mg. | 54.2 × |
| 10. | 1.955 mg. | 4.008 mg. | 55.8 |
| 11. | 2.254 mg. | 4.618 mg. | 55.9 |
| 12. | 2.512 mg. | 5.083 mg. | 55.2 |
| 13. | 2.484 mg. | 5.042 mg. | 55.3 |
| 14. | 2.346 mg. | 4.819 mg. | 55.9 |
| 15. | 1.895 mg. | 3.842 mg. | 55.3 |
| 16. | 1.792 mg. | 3.635 mg. | 55.2 |

× N.B.  The bad results are all low, hence they cannot be caused by incomplete decomposition of oxides of Nitrogen.

CARBON AND HYDROGEN IN COMPOUNDS FREE OF NITROGEN.

| Compound. | Carbon | | Hydrogen | |
|---|---|---|---|---|
| | Found Per Cent. | Required Per Cent. | Found Per Cent. | Required. Per Cent. |
| Oxalic acid. | 18.9 | 19.1 | 4.68 | 4.76 |
| | 19.0 | | 4.59 | |
| Lactose | 39.9 | 40.0 | 6.60 | 6.67 |
| | 39.9 | | 6.55 | |
| | 39.8 | | 6.52 | |

In conclusion may I take this opportunity of conveying my sincerest gratitude and appreciation to Professor G. G. Henderson, F.R.S., Chief of the Department of Chemistry in the University of Glasgow, and Dr David T. Gibson, my supervisor, for their helpfulness and interest in matters relating to my work.

*J. Hume Caulfield.*

The University,
Glasgow.

# BIBLIOGRAPHY.

1. Vieböck, Ber., 1932, 496.

2. Friedrich, Pregl, "Quantitative Org. Micro analysis", p.163 (1930).

3. Pregl's "Quantitative Org. Micro analysis." 2nd Eng. Ed. 30.

4. "                "              "      "        "          "    "      " 118.

5. Kneitsch. Ber. 34.  4069-4115. (1901)

6. Pregl. "Quant. Org. Micro Analysis". 2nd. Eng. Edn. 102.

7. Vieböck, Ber. 1932, 495.

8. Cowie & Gibson.  Analyst. 1934, 59, 388.

9. Volhard.  Annalen 1878.  24, 190.

10. Mohr.  Annalen 1856.  97, 335.

11. Fajans & Frankenburger.  Zeit. Physik. Chem. 1923. 105, 225.

12. Berend.  Biochem. Zeitschrift 252. Bd. 4-6 Ht. 362-5. 1932.

13. Votecek.  Chem. Zeit 1918.  64, 1-14.

14. Jurecek.  Czeck. Chem. Comm., Coll. vii, No.7, 1935. 316-318.

15. Tarvin, Todd, and Boswell.  J. Amer. Water Works Assoc., 1933, 25, 1645.

16. Strebinger and von Zombory.  Z. anal. Chem., 1930, 82, 806.

17. Schroeder, J.  Ind. Eng. Chem., Anal. Ed., 1933, 5. 403 Abst. Analyst 1934, 59. 134.

18. Sheen & Kahler.  J. Ind. Eng. Chem., Anal. Ed., 1936, 8, 127-130.

19. Muer, J. Ind. Eng. Chem., Anal. Ed., 1911, 3, 553. Abst. Analyst 1911, 36, 519.

20. Fiske.  J. Boil Chem. 47, 59 (1915).

21. Drummond.  J. Biol. Chem. 47 (1915).

22. Emich.  Pregl's "Quant. Org. Micro. Anal." Eng. Ed. 2nd.p.108.

23. Vieböck and Schwappach Ber., 1930. 63, 2818.

24. Vieböck and Brechar. Ber., 1930, 63, 3207.

25. Arndt & Martius, Annalen. 1932, 499, 269.

26. Lieb. Pregl's "Quantitative Org. Micro Analysis" Eng. Edn.,
    p. 156.

27. Guillemet. Bull. Soc. Chimique de France. 1932, 51, 1547.

# Micro-Volumetric Determination of Sulphur in Organic Compounds containing Halogen and Nitrogen

BY

D. T. GIBSON, D.Sc., and T. H. CAULFIELD, B.Sc., A.I.C.

# Micro-Volumetric Determination of Sulphur in Organic Compounds containing Halogen and Nitrogen

BY D. T. GIBSON, D.Sc., AND T. H. CAULFIELD, B.Sc., A.I.C.

COWIE and Gibson[1] showed that the combustion-volumetric determination of sulphur could be combined with that of chlorine, and the two elements satisfactorily determined by acidimetric followed by argentimetric titration.

Their process is greatly improved by the use of Vieböck's[2] mercuric oxycyanide for the halogen determination, which is resolved into an ordinary acidimetric titration with a sharp end-point.

At the same time we have taken the opportunity of introducing several other simplifications:—(i) The tube is maintained at a temperature of 400° C. electrically. (ii) The contact is a length of 80-mesh Pt/Rh gauze rolled into the form of a tube. (iii) There is affixed to the tube a 50-ml. distilling flask, the side-arm of which is bent bow-shaped, and has mid-way along its length a bulb blown.

Before attaching the flask, a boat containing about 8 mg. of sodium bicarbonate is introduced into it. The alkali is dissolved in 1 ml. of water, and 0·04 ml. of perhydrol is added. This solution is sucked up into the beads. The flask is then rotated so that the side-arm is in a horizontal position, and 0·04 ml. of perhydrol and 0·20 ml. of $N/100$ alkali are pipetted into the arm. This forms a seal which is broken intermittently by the oxygen flow.

After combustion, the products of oxidation are washed into the (receiving) flask, and the total acidity of the solution is found by titration with $N/100$ sulphuric acid.

The solution is now concentrated to 2 to 3 ml., 10 ml. of a saturated solution of mercuric oxycyanide are added, and the halogen-content is determined by titration with $N/100$ sulphuric acid, and hence by difference sulphur may be estimated.

The equation

$$2Hg(OH)(CN) + 2NaCl \rightleftharpoons HgCl_2 + Hg(CN)_2 + 2NaOH$$
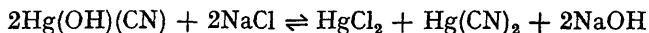
represents the condition of the solution for the determination of halogen. In concentrated solution equilibrium lies practically quantitatively to the right, and the sodium hydroxide may be titrated with acid other than halogen acid. Dilution of the solution shifts the equilibrium to the left, and it is therefore necessary to arrange conditions so that the acid does not add unduly to the dilution, or results will be low.

With bromides the degree of accuracy is equally good.

| Compound | Sulphur | | Chlorine | |
|---|---|---|---|---|
| | found Per Cent. | required Per Cent. | found Per Cent. | required Per Cent. |
| Dichlorobenzene, $C_6H_4Cl_2$ | | | 48·3, 48·4 | 48·3 |
| Tetrachlorodiphenyl disulphoxide, $C_{12}H_6O_2S_2Cl_4$ | 16·5 | 16·5 | 36·7 | 36·5 |
| Chlorophenylsulphonacetone, $C_9H_9O_3SCl$ | 13·6 | 13·5 | 15·3 | 15·1 |
| Ethyl chlorocamphorsulphonate, $C_{12}H_{18}O_3SCl$ | 11·4 | 11·5 | 12·5 | 12·1 |
| Dichlorophenylsulphone, $C_{12}H_8O_2SCl_2$ | 11·1 | 11·3 | 25·2 | 25·1 |
| Tetrachlorodiphenyl disulphide, $C_{12}H_6S_2Cl_4$ | 17·7 | 17·9 | 39·4 | 39·9 |
| Naphthalene sulphonchloride, $C_{10}H_7O_2SCl$ | 14·0 | 14·2 | 15·8 | 15·7 |
| Toluenesulphonchloride, $C_7H_7O_2SCl$ | 16·4 | 16·8 | 18·5 | 18·1 |

| Compound | Sulphur | | Bromine | |
|---|---|---|---|---|
| | found Per Cent. | required Per Cent. | found Per Cent. | required Per Cent. |
| Ethyl bromocamphorsulphonate, $C_{12}H_{18}O_3SBr$ | 9·69 | 9·94 | 24·6 | 24·8 |
| Bromophenylmethylsulphone, $C_7H_7O_2SBr$ | 13·9 | 13·6 | 34·0 | 34·0 |
| $CH_3OC(CH_3)_2SO_2C(SO_2Me)Br_2$ | 16·2 | 16·5 | 40·8 | 41·2 |
| $CH_2-SO_2$  $CH_3$ (structure) | 24·0 | 24·4 | 29·9 | 30·4 |
| Tolyldibromopropylsulphone, $C_{10}H_{12}O_2SBr_2$ | 9·28 | 9·00 | 45·8 | 45·0 |

For compounds containing nitrogen, Friedrich[3] has proposed a volumetric method for determining sulphuric acid; it is based on the stability of potassium bisulphate.

We have applied this to artificial mixtures of nitric and sulphuric acids, with the following results:

| Nitric acid (0·0170 $N$) ml. | Sulphuric acid (0·00912 $N$) ml. | Sodium sulphate (0·0210 $N$) ml. | Alkali found (0·0113 $N$) ml. | Alkali required (0·0113 $N$) ml. |
|---|---|---|---|---|
| 1·00 | 3·00 | 5·00 | 2·49 | 2·48 |
| 3·00 | 3·00 | 5·00 | 2·50 | 2·48 |
| 1·00 | 3·00 | 6·00 | 2·50 | 2·48 |
| 3·00 | 3·00 | 6·00 | 2·50 | 2·48 |
| 2·00 | 3·00 | 8·00 | 2·50 | 2·48 |
| 5·00 | 3·00 | 6·00 | 2·50 | 2·48 |
| — | 3·00 | 10·00 | 2·50 | 2·48 |

When the method was applied to products of combustion of compounds containing sulphur, the results were always 1 to 3 per cent. low. For example, the following results were obtained with propylene diphenylsulphone ($C_{15}H_{16}O_4S_2$):

| Sulphur (direct titration) | Sulphur (after Friedrich) | | Sulphur (required) |
|---|---|---|---|
| Per Cent. | Per Cent. | Per Cent. | Per Cent. |
| 19·6 | 18·6 | 18·4 | 19·8 |
| | 17·9 | 17·0 | |

As the discrepancy was probably due to incomplete conversion of $SO_2 \rightarrow SO_3$ by perhydrol, chlorine water was substituted. Here the results were variable, sometimes tending to be high, owing to retention of hydrochloric acid (as indicated by silver nitrate), which caused us to reject the method.

| Compound | Sulphur found Per Cent. | Sulphur required Per Cent. |
| --- | --- | --- |
| Propylenediphenylsulphone | 19·7 | 19·8 |
| Toluenesulphonamide | 18·6 | 18·7 |
| Thiourea | 42·3 | 42·1 |
| Dinitrodiphenyl disulphide | 20·0 | 20·8 |
| 4-Chloro-3-nitro-4'-2' dinitrodiphenylsulphone | 6·25 | 8·21 |
| Nitrodiphenyl sulphide | 15·7, 13·4 | 13·8 |

Other methods tried and subsequently discarded (for reasons indicated in parenthesis) included potassium palmitate [(Halm, Vieweg and Meyer),[4] (variable $p$H)]; rhodizonic acid [(Strebinger and Von Zombory[5]) (satisfactory for $N/10$ solution, not for $N/100$)]; tetrahydroxyquinone [(Schroeder[6]) (for the same reasons as rhodizonic acid)]; and benzidene [(Muer)[7] (occlusion, giving high results)].

A method based on the use of barium chloride and potassium chromate was found to be a distinct improvement on others, and was finally adopted.

| Compound | Sulphur found Per Cent. | Sulphur required Per Cent. |
| --- | --- | --- |
| Propylenediphenylsulphone, $C_{15}H_{16}O_4S_2$ | 19·5 | 19·8 |
| Camphor sulphonylmethylsulphonylmethane, $C_{12}H_{20}O_4S_2$ | 21·2 | 20·8 |
| Benzyl sulphonylmethylsulphonylmethane, $C_9H_{12}O_4S_2$ | 25·7 | 25·9 |
| Thiourea, $CH_4SN_2$ | 42·8 | 42·1 |
| ,, ,, | 42·3 | 42·1 |
| Dinitrodiphenyl disulphide, $C_{12}H_8O_4S_2N_2$ | 20·6 | 20·8 |
| Toluenesulphonamide, $C_7H_9O_2SN$ | 18·4 | 18·7 |
| Cystine, $C_6H_{12}O_4S_2N_2$ | 26·6 | 26·7 |
| Nitrodiphenyl sulphide, $C_{12}H_9O_2SN$ | 13·8 | 13·8 |
| Sulphanilic acid, $C_6H_7O_3SN$ | 18·5 | 18·5 |
| Thiocarbanilide, $C_{13}H_{12}SN_2$ | 14·1 | 13·9 |
| Phenyl-sulphonyl-acetonitrile, $C_8H_7O_2SN$ | 17·4 | 17·7 |
| ,, ,, ,, | 17·5 | 17·7 |
| 4-Chloro-3-nitro, 2'-nitro-4'-nitro-diphenylsulphone, $C_{12}H_6O_8SN_3Cl$ | 8·25 | 8·25 |
| 4-Bromo-3-nitro-2'-nitro-4'-nitrodiphenylsulphone, $C_{12}H_6O_8SN_3Br$ | 7·27 | 7·41 |
| 4-Chloro-2'-nitro-4'-nitro-diphenylsulphone, $C_{12}H_7O_6SN_2Cl$ | 9·11 | 9·37 |

The combustion of the compound was carried out in an ordinary Pregl tube heated to 400° C. The improved Pt/Rh contact was used. A pre-catalyst of platinum foil was also employed. This was heated to a temperature between 500° to 600° C., to promote the disruption of the compound. The beads were moistened with distilled water only. The products of combustion were washed into a receiver and neutralised with $N/100$ alkali. The sulphate was precipitated in hot neutral solution by drop-wise addition of barium chloride solution ($N/100$).

The excess of barium chloride was precipitated with potassium chromate solution, and the combined sulphate and chromate precipitates were filtered off and

washed on an Emich filter-stick. The filter-stick was then washed and boiled in dilute hydrochloric acid solution. The solution was cooled, potassium iodide was added and the liberated iodine was titrated with $N/100$ thiosulphate solution. The determination can be complete in less than 2 hours.

The preliminary alkali titration varies, but it gives an upper limit to the acidity of the solution, and hence a measure of the volume of barium chloride solution required.

The excess of the total acidity over the sulphur acidity varies by from 5 to 20 per cent. of the latter for the sulphur-nitrogen-compounds analysed, whilst for the sulphur-nitrogen-halogen-compounds it rises to over 100 per cent.

### REFERENCES

1.  D. W. Cowie and D. T. Gibson, ANALYST, 1934, **59**, 388.
2.  F. Vieböck, *Ber.*, 1932, 496.
3.  A. Friedrich, Pregl, *Quantitative Organische Mikroanalyse*, 3rd Ed., p. 163 (1930).
4.  F. L. Halm, K. Vieweg and H. Meyer, *Z. anorg. Chem.*, 1923, **126**, 257.
5.  R. Strebinger and L. von Zombory, *Z. anal. Chem.*, 1930, **82**, 806.
6.  W. C. Schroeder, *Ind. Eng. Chem., Anal. Ed.*, 1933, **5**, 403; Abst., ANALYST, 1934, **59**, 134.
7.  H. F. Muer, *J. Ind. Eng. Chem.*, 1911, **3**, 553; Abst., ANALYST, 1911, **36**, 519.

CHEMISTRY DEPARTMENT
   GLASGOW UNIVERSITY

substance, but, in disagreement with them, we find that with such quantities the blank given by the absorbing solution is significant and is seriously increased by time, temperature, dilution with water, and even by illumination.

After the decomposition, Vieböck washes the absorbing solution into a conical flask containing ½—1 g. of dissolved sodium acetate, destroys the excess of bromine with 4 or 5 drops of formic acid, adds 0·1—0·2 g. of potassium iodide, acidifies the solution with sulphuric acid, and titrates it with thiosulphate. He suggests that the presence of undissolved sodium acetate gives rise to bromate formation; but we consider it more likely that the discrepancy arises from deficiency of dissolved acetate. Further, we found it necessary to use excess of sulphuric acid for the liberation of total iodine.

We find that a solution of bromine in potassium bromide obviates these difficulties and recommend the following modifications.

An amount of material corresponding to 3—10 c.c. of $N/50$-thiosulphate should be taken. The " Verschlussstäbchen " should fit tube A as tightly as possible without seizing (cf. Pregl, 3rd German Edition, p. 199).

A very small flame within 1 cm. of the flask gives better control of the heating than does a glycerol-bath (Vieböck). Heating should be continued for 40 minutes, *i.e.*, 5 minutes after bumping begins.

As little washing solution as possible should be used. A saturated solution of sodium bicarbonate is efficient.

The absorbing solution should be freshly prepared by adding 6 drops (0·05 c.c.) of bromine to 18 c.c. of 20% aqueous potassium bromide. Half of this serves as a blank, and is kept beside the absorption tubes during the estimation, being titrated under the same conditions at the end. The remaining absorption solution is filled into two absorption tubes (cf. Pregl, *op. cit.*, p. 207, Fig. 36), 7·5 c.c. into the first, 1·5 c.c. into the second. The absorption tubes and the blank are immersed in ice-water during the estimation.

When the decomposition is complete, the two absorbing solutions are washed into a conical flask with 45 c.c. of 25% potassium acetate, and decolorised with 1 c.c. of 85% formic acid. 2 C.c. of 10% potassium iodide and 25 c.c. of $5N$-sulphuric acid are added, and the iodine titrated with $N/50$-sodium thiosulphate. The blank, similarly treated, does not exceed 0·10 c.c.

The following results were obtained :

| Substance. | Wt., mg. | OMe, %. | | Substance. | Wt., mg. | OMe, %. | |
|---|---|---|---|---|---|---|---|
| | | Found. | Calc. | | | Found. | Calc. |
| Vanillin | 0·544 | 20·5 | 20·4 | *p*-Methoxybenzaldoxime | 2·349 | 20·2 | 20·5 |
| | 0·802 | 20·2 | — | | 2·845 | 20·6 | — |
| | 1·318 | 20·2 | — | Papaverinol | 3·854 | 34·6 | 34·9 |
| | 2·017 | 20·3 | — | *p*-Methoxybenzylideneaceto- | 3·294 | 12·9 | 13·0 |
| | 2·498 | 20·4 | — | phenone | | | |
| | 3·100 | 20·4 | — | Dibenzoyl *p*-toluenesulphonyl | 4·241 | 5·61 | 5·57 |
| | 3·216 | 20·3 | — | methylglucoside | 3·849 | 5·61 | — |
| | 3·592 | 20·2 | — | Iododibenzoyl *p*-toluene- | 4·610 | 5·02 | 4·55 |
| | 4·198 | 20·3 | — | sulphonyl methylglucoside | 4·613 | 5·02 | — |
| | 4·603 | 20·2 | — | Tetramethyl α-methyl- | 1·741 | 60·9 | 62·0 |
| | 4·693 | 20·1 | — | glucoside | | | |
| α-Methyl- | 3·472 | 16·2 | 16·0 | | | | |
| glucoside | 3·771 | 16·1 | — | | | | |
| | 3·890 | 16·1 | — | | | | |

Low results were obtained if (i) only one receiver was used; (ii) the heating lasted less than 40 minutes; (iii) the titration was too large.

### 343. *Microvolumetric Determination of Methoxyl.*

By DAVID T. GIBSON and THOMAS H. CAULFIELD.

VIEBÖCK and SCHWAPPACH (*Ber.*, 1930, **63**, 2818) have shown that Pregl's methoxyl estimation can be effected volumetrically by absorbing the alkyl iodide in a solution of bromine, destroying excess of bromine, adding potassium iodide, and titrating the iodine liberated, according to the scheme $CH_3I \longrightarrow CH_3IBr_2 \longrightarrow IBr \longrightarrow HIO_3 \longrightarrow 3I_2$. Arndt and Martius (*Annalen*, 1932, **499**, 269), who used this method with a series of sulphur and nitrogen alkoxy-derivatives, found it very satisfactory with 25—50 mg. of material.

Vieböck and Brecher (*Ber.*, 1930, **63**, 3207) also described a procedure for 1—5 mg.