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HW-17046

Chemistry - General

THE COULOMETRIC DETERMINATION
OF ACID

by

W. N. Carson, Jr
and
Roy Ko
Analytical Section
Technical Services Division

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THE COULOMETRIC DETERMINATION
OF ACID

Introduction

The need for a method of acid determination which could be used for small samples and easily adapted to remote control led to the investigation of the use of electrolytically generated base for the titration of acid in certain solutions. The use of electrolytically generated base for the titration of acetic acid in the presence of nitric acid has been reported (1).

Summary

The use of electrolytically generated base is feasible for acid titrations by coulometric methods of analysis. In general, those solutions which can be titrated with standard solutions can also be titrated coulometrically. Precision and accuracy for microsamples are as good or better than those obtained by use of burets and standard solutions. In addition, a direct reading for the determination can be obtained and the apparatus is easily adapted to remote control. Preliminary work has indicated that generation of acid for base titration is also feasible.

ACID DETERMINATION

Generation of Base

The electrical equipment used is described in a previous report (2) which gives the construction of the constant current source and the operation of the coulometer system. The indicator systems used are conventional and will not be described in detail.

Base can be generated by several different schemes. One is to separate the anode and cathode by a salt bridge. The cathode reaction is:

hydrogen ion is removed from the solution. This is equivalent to the addition of base and has been found to be a feasible system (1). However, the salt bridge has a relatively high resistance, is fragile, and easily loses the gelatin or agar-agar binder which causes cross-contamination of the samples. For these reasons its use is not desirable.

All these difficulties are avoided if both anode and cathode are placed in the titration cell. To avoid the mere electrolysis of water by such a system, i.e.,

SECRET

a means of preventing oxygen evolution is necessary. This can be accomplished by using an anode that will dissolve at a potential below that necessary for oxygen evolution. The most suitable electrode of this type found to date is one of aluminum which, however, permits oxygen evolution at other than very low current densities. Addition of fluoride removes this difficulty, but introduces the buffering action of fluoride which is to be avoided, if possible, in acid-base work.

Another means of avoiding oxygen evolution is to use a halide electrolyte and deposit the halide on a silver or mercury electrode as an insoluble precipitate. This scheme is the basis of the method here reported. The reactions are as follows:

It is seen that this is again the destruction of hydrogen ion in the solution.

The silver and mercury electrodes must be cleaned after a few runs because the resistance of the precipitate causes the voltage of the electrode to increase to a value such that oxygen evolution at the anode is observed which results in less than 100% current efficiency in the electrolysis. Silver electrodes are cleaned in cyanide solution; mercury electrodes by mechanical removal of the film. Mercury electrodes are a new type and no data is reported on them in this report.

Calculator

A calculator can be put into the electrical system since a constant current is used for the titration. The number of equivalents of base generated is proportional to the number of coulombs used, which is, under the condition of constant current, proportional to the time of generation. Hence, the amount of acid titrated is proportional to the time. All that is required for a direct reading of the acid value is to set the current to a value such that the time units are equal to the units in which the acid value is desired. For example, if the acid value is to be reported in grams per liter of nitric acid and the time unit is one minute, the value of the current necessary to make one minute of titration time equivalent to one gram per liter of nitric acid is calculated as follows:

$$\text{g/L} = \frac{1 \times t}{F} \times \frac{\text{HNO}_3}{S} \times 10^6 \quad \text{or}$$

$$\text{g/L} = \text{equivalents of base generated} \times \frac{\text{equivalent weight of HNO}_3 \times 10^6}{\text{sample in microliters}}$$

where i = current in amperes
 t = time in seconds
 F = faraday = 96,500 coulombs
 HNO_3 = equivalent weight of nitric acid = 63.02g
 $\text{g/L} = t/60$ (by condition of operation)
 S = sample size in microliters

Solving for i ; $i = 0.00002553 \times S$ amperes
 $i = 0.02553 \times S$ milliamperes

Procedure

The procedure varies with the type of sample, but in general consists of taking the sample, diluting to 3-10 ml, and adding a halide electrolyte (sodium chloride or sodium bromide) and a complexing agent, if needed. No dilution occurs during titration. If a colorimetric endpoint is to be used, indicator is added. The electrodes (platinum cathode and silver anode) are inserted into the titration vessel. These are most conveniently taken as single wires. After starting the stirrer, the generator is turned on and the titration proceeds. If a pH meter is used to determine the endpoint, it has been found necessary to shut off base generation while taking a reading unless special care has been taken to shield the glass electrode. At the endpoint, 10 or 5 second intervals are used, and the time of the endpoint is found by interpolation (1).

Results

Table I gives the precision and accuracy data of the method as obtained from several different samples. Interferences studied were uranium and lead. Various complexing agents for lead were tried; the table includes some of the more successful. Oxalate was used to complex the uranium. In the table the type of base generation is indicated by "sep" for the systems in which the cathode and anode are separated by a salt bridge and "Pt-Ag" for the system in which a platinum cathode and silver anode is used. The indicator system used is given by "glass electrode" for the potentiometric experiments and by the name of the indicator for the visual endpoint experiments.

BASE DETERMINATION

Generation of Acid

Generation of acid is easily accomplished by use of the separated compartment cell if halide is absent from the anode compartment (1). The reaction is as follows:

Halides interfere because free halogen is evolved with the oxygen at the anode.

A two electrode system, platinum anode and silver-silver bromide cathode, can be used. The behavior of this system is still under investigation, but it is not as satisfactory as the separated system.

Another two electrode system has been successfully used. This is the method of Szébellédy and Somogi (3), which consists of using an electrolyte of sodium bisulphite and sodium bromide with bromocresol green indicator. Two platinum electrodes are used in a single compartment. The reactions are as follows:

The bromine reacts further:

This appears at first glance to be merely the oxidation of bisulphite. However, a bisulfite solution is neutral to the indicator bromocresol green. If base is added to this solution, the indicator assumes the basic color, and as soon as the base is neutralized by the bisulphate (a strong acid) the next small amount of bisulphate gives the acid color of the indicator. This system works on those samples that give a basic color when added to the bisulphite-bromide-indicator electrolyte.

W. N. Carson, Jr.
W. N. Carson, Jr.
Analytical Section
Technical Services Division

Roy Ko
Roy Ko
Analytical Section
Technical Services Division

References

- (1) Carson, W. N., Jr., and Ko, Roy, "The Coulometric Determination of Acetic Acid", HW-13301.
- (2) Carson, W. N., Jr., "The Coulometric Determination of 8-Hydroxyquinoline", HW-13300.
- (3) Szébellédy, L. and Somogi, Z., Z. anal. Chem., 112, 385 (1938).

SECRET

TABLE I

COULOMETRIC TITRATION OF HNO_3 BY ELECTROLYTICALLY GENERATED BASE

Sample	g/L Added	Average g/L Found	Sample Size μl	No. of Determinations	% Precision (99% Limits)	Type of Base Generation	Electrolyte	Indicator
Dilute HNO_3	6.304 19.53	6.276 19.40	200 200	5 5	± 2.48 ± 0.92	Sep. Sep.	0.01 N KCl 0.02 N KCl	Methyl Red Phenolphthalein
81% HNO_3	810.0 810.0 195.9 195.9 195.9	810.8 815.7 193.3 185.1 186.9	5 1 10 10 10	5 12 5 5 7	± 0.06 ± 4.6 ± 7.0 ± 1.2 ± 5.9	Sep. Sep. Sep. Sep. Pt-Ag	0.05 N KCl 0.05 N KCl 0.02 M Na_2SO_4 0.04 M KIO_3 0.1% Versene*	Glass Electrode Glass Electrode Glass Electrode Glass Electrode Thymol Blue
3 M HNO_3 + 0.15 M $\text{Pb}(\text{NO}_3)_2$	195.9 195.9 195.9 195.9	196.9 195.2 195.1 195.3	10 10 10 10	9 5 4 12	± 5.6 ± 1.2 ± 2.7 ± 2.3	Pt-Ag Pt-Ag Pt-Ag Pt-Ag	1% NaCl 0.1% Versene* + 1% NaCl 0.1% Versene* + 1% NaCl 1% NaCl	Cresol Red + Thymol Blue Methyl Red Cresol Red Cresol Red
1.2 M HNO_3	98.25	103.0	10	3	± 0.8	Pt-Ag	1% $\text{Na}_2\text{C}_2\text{O}_4$ 1% NaBr	Glass Electrode
1.2 M HNO_3 + 1000 g/L UNH	98.25	99.2	10	3	± 3.3	Pt-Ag	1% $\text{Na}_2\text{C}_2\text{O}_4$	Glass Electrode
0.6 M HNO_3 + 1000 g/L UNH	49.13	50.3	10	4	± 13.8	Pt-Ag	1% $\text{Na}_2\text{C}_2\text{O}_4$	Glass Electrode
0.48 M HNO_3 + 1000 g/L UNH	39.30	39.9	10	2		Pt-Ag	1% $\text{Na}_2\text{C}_2\text{O}_4$	Glass Electrode

*Versene is the trade name of Sodium Ethylenediaminetetracetate.

HW-17046

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