REMARKS ON DIFFERENT METHODS FOR ANALYZING TRONA AND SODA SAMPLES

Gülay ATAMAN*; Süheyla TUNCER* and Nurgün GÜNGÖR*

ABSTRACT. — Trona is one of the natural forms of sodium carbonate minerals. It is well known as «sesque carbonate», «urao» or «trona» in the chemical literature, and the chemical formula of the compound is [$Na_2CO_3.NaHCO_3.2H_2O$]. The aim of this work is to adapt the standard methods for the analysis of trona samples, considering the interferences arising from silicates and other minerals found together with trona samples. In order to reduce the experimental errors, the analyses used for the determination of trona samples have been revised. The experimental results using potentiometric titration, $AgNO_3$ external indicator and $BaCl_2$ titration methods have been compared to theoretical results using statistical evaluations. 95 % confidence level, which is commonly used by analytical chemists, was employed as the basis of evaluation, R values, $\frac{\text{Student's t calculated}}{\text{Student's t tabulated}}$ at 95 % confidence level of 7 trona samples from Beypazarı, for the percentages of Na_2CO_3, were found to be 0.008 in $BaCl_2$ method, 3.25 for $AgNO_3$ external indicator method and 3.26 for potentiometric method; for the percentages of $NaHCO_3$ the same values are 0.59 for $BaCl_2$ method, 2.83 for $AgNO_3$ external indicator method and 3.59 for potentiometric method. Systematic error is indicated when R> 1. In addition to quantitative analysis of trona samples, qualitative XRD analyses have been routinely performed for each sample and the results were found to be in good agreement.

INTRODUCTION

Trona is a naturally occuring from of sodium carbonate minerals. It may be named as «sesque carbonate», «urao» or «trona» the general formula for the compound is [Na_2CO_3. $NaHCO_3$. $2H_2O$]. A double salt of sodium carbonate-sodium bicarbonate, trona is soluble in water. Crystals of this mineral is transparent or white, the color darkens with increased impurities. Its density is 2.1 g/cm^3 and hardness is 2.5-3 on Mohs scale.

Production of soda ash from trona is somewhat simpler than Solvay or Leblanc processes and can be accomplished at a lower cost. Solvay or Leblanc processes are well described in literature (1). Two variations of production of soda ash from trona are in use. One starts by dissolving trona ore (trona process); the other first calcines trona and then dissolves the crude soda ash thus produced (monohydrate process) (2). In both processes production of soda is particularly simple.

Sodium carbonate is one of the basic chemicals, and increase in its usage generally is parellel to the economical growth. Sodium carbonate is commonly employed in glass and ceramic, petroleum, aluminium, paper industries, manufacture of soap and detergents, in the production of caustic soda and sodium nitrate, ferreous and non-ferrous metallurgical processes.

The first natural resources of trona were discovered in the United States; initially in the west later in Green River, Wyoming (2). The other important resources are Mogadi Lake in Kenya and Texaco underground brines in Mexico. Ninety percent of world's production comes from the United States of America. In 1939, seventeen Solvay factories were actively operating in the U.S.A. Today only one of these is in operation, the rest have been replaced by natural soda. In Europe, however, the dependency on solvay process is still valid as no significant resources have been discovered.

TRONA RESOURCES IN TURKEY

Natural soda in Turkey, is present in lake Van and lake Arm which is nearby the former. The concentration of soda in lake water, however, is low and the time available for the use of solar energy is only 2-3 months per year; therefore soda production is not economical at the present time.

The first trona deposit in Turkey was found by Mineral Research and Exploration Institute (MTA) around Beypazarı, during coal exploration studies. The studies showed that trona is present 130-140 m deep, in layers which are thicker and richer in quality compared to the ones in the U.S.A. The results obtained from only such a limited area indicated the presence of nearly 200 million tons of trona. This reserve may be small in comparison to 50 billion tons reserve in Wyoming (U.S.A.). However, exploration activities in the same area show that discovery of new orebodies is possible. Such a resource will allow the production of chemicals such as "soda, sodium hydroxide and other sodium derivatives for about a hundred years. The resource which was found by MTA has been transferred to Etibank.

Scope of the work

The main purpose in trona analysis is the quantitative determination of water soluble carbonates. In most cases, however, trona is also present in clays and other minerals. Despite this fact, analytical methods were not developed considering these matrix conditions. The kind and quantity of clays and other carbonate compounds not seperated from aqueus phase, require different kind of analytical methods. The purpose of this study has been the application of several analytical methods on core samples obtained from Beypazarı trona field. Investigations have been carried out in order to eliminate several analytical interferences affecting the accuracy of the results.

General information on analytical methods

X-ray diffraction spectrometry (XRDS) was used for qualitative analysis of samples, where other analytical methods were employed for quantification.

X-ray diffraction spectrometry: XRDS is a common method to determine the kind of minerals. The principle is the determination of the distances between crystal layers, employing the diffraction of X-rays of known wavelength, a diffractometer is used for analysis.

Other Analytical Methods: Two basic aims of the study were to find out the percentage of trona and determination of impurities. The analytical methods applied for these purpose are listed below.

Determination of trona percentage

a. Total alkalinity-potentiometry
b. Na_2CO_3 percentage-calculation by (a) and (c)
c. $NaHCO_3$ percentage-potentiometry, volumetry ($AgNO_3$ and $BaCl_2$ methods)

Determination of impurities

a. Water insoluble content (ASTM, 1980)
b. SO_4 determination-Gravimetry (ASTM, 1980)

c. Cl determination-Mohr method (ASTM, 1980)

d. Ca++ and Mg++ determination-EDTA complexometry (ASTM, 1980)

Basic features of analytical methods used are given in «Experimental section».

EXPERIMENTAL

Reagents and solutions

All analytical reagents were of analytical purity. Deionized water used, contained all the species determined below their detection limits. All the solutions were prepared according to the directions in the references given below.

Instrumentation

A Jeol JDX-8P spectrometer with a Cu source operated at 40 kV and 20 mA, Ni filter were used for instrumentation.

For potentiometric measurements, initially a system consisting of a Corning Model pH-meter with a peristaltic pump, magnetic stirrer and a strip chart recorder was used. In later stages of the study, a TOA HSM 10A fully automatic titrator and finally Fisher model CAT automatic titrator with a microprocessor control were employed to further verify the results.

Conventional burettes and other glassware were used for $AgNO_3$-external indicator, $BaCl_2$, Mohr's and EDTA complexometric methods. Gravimetric determinations were realized by necessary conventional apparatus.

Preparation of samples

Solid samples were dried at 30°C and powdered prior to XRD analysis. For other analytical methods, samples were powdered and dried at 30°C and was dissolved in deionized water to yield a 20 g/1 solution; after standing overnight, aliquots were drawn from this solution for analyses.

Analytical methods

For determination of trona percentage, the methods applied and their fundamental principles are given below and the, necessary adaptations have been made.

1. Potentiometry (Skoog, 1969)
2. $BaCl_2$ volumetric titration (Monographs, 1981)
3. $AgNO_3$ titration with external indicator (ASTM, 1980)
4. X-ray diffraction spectrometry

1. Potentiometric method. — Trona samples were titrated with 0.1 N HC1; and total alkalinity was calculated from second endpoint where carbonate and bicarbonate contents were calculated by using first endpoint. A titration curve and endpoints of a trona solution is given in Figure 1. In addition, the studies were carried out on pure Na_2CO_3 and synthetic Na_2CO_3-$NaHCO_3$ mixtures, clay+trona and finally dolomite ($CaCO_3$+$MgCO_3$) +clay+trona mixtures, in order to investigate on possible interferences in this method.

2. $BaCl_2$ volumetric titration method. — The principle in this method is transformation of bicarbonate ions into carbonate by NaOH, precipitation as $BaCO_3$ by $BaCl_2$, and back titration of excess NaOH by acid. Concentration of bicarbonate is this determined. Carbonate content is found by calculation using also total alkalinity values.

3. $AgNO_3$ titration with external indicator. — The principle in this method is the determination of bicarbonate ions using NaOH as a titrant and $AgNO_3$ as an external indicator. Carbonate content is found by calculation using also total alkalinity values.

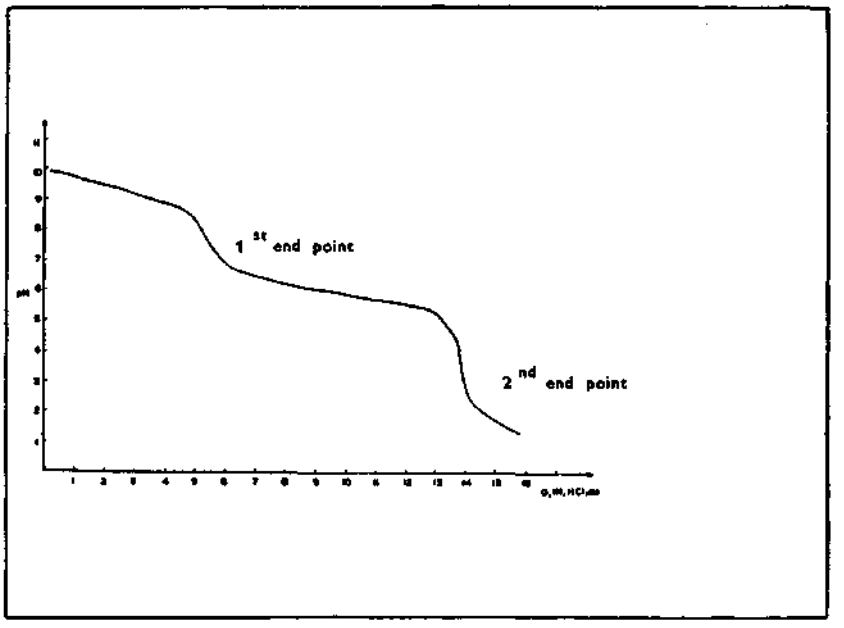

Fig. 1 - The endpoints in potentiometric titration of a trona sample with hydrochloric acid.

Appendix 1 — Some definitions for trona analysis

Total alkalinity : This represents the total of CO^{2-}_3 and HCO^{-}_3 ions contained by water soluble part of the sample, in terms of Na_2O and Na_2CO3. This corresponds to total of Na_2CO_3 and $NaHCO_3$.

Example :

A sample which consists of 100 % trona, has a total alkalinity of
41.13 as Na_2O %, or
70.34 as Na_2CO_3 %

Na_2CO_3 % value : This corresponds to the real Na_2CO_3 as weight percentage in the sample.

Example :

A sample which consists of 100 % trona; has a Na_2CO_3 % value of 46.89.

$NaHCO_3$ % value : This value corresponds to the real $NaHCO_3$ as weight percentage in sample.

Example :

A sample which consists of 100 % trona has a $NaHCO_3$ % value of 37.16.

Trona % value : When the sample is known to be trona, this is a value as calculated from «total alkalinity».

Example :

For a sample which contains trona and possibly clay and other compounds, if total alkalinity is 41.13 % as Na_2O, trona % value should be 100.

Appendix 2 — Other minerals coexist with trona in Ankara-Beypazarı samples

Mineral	*Formula*
Trona	$Na_2CO_3.NaHCO_3.2H_2O$
Pirssonite	$Na_2CO_3.CaCO_3.2H_2O$
Gaylussite	$Na_2CO_3.CaCO_3.5H_2O$
Nahcolite	$NaHCO_3$
Thermonatrite	$Na_2CO_3.H_2O$
Brugnatellite	$Mg_6FeCO_3(OH)_{13}.4H_2O$
Natron	$Na_2CO_3.10H_2O$
Mirabilite	$Na_2SO_4.10H_2O$
Thenardite	Na_2SO_4
Glauberite	$Na_2SO_4.CaSO_4$
Dolomite	$CaCO_3.MgCO_3$
Analcite	$Na_2O.Al_2O_3.4SiO_2.2H_2O$

Appendix 3 — Some conversion factors employed in evaluation of trona analysis results

Result given	×	*Factor*	=	*Result sought*
Na_2CO_3		.58483		Na_2O
Na_2CO_3		2.1324		Trona
Trona		.41139		Na_2O
Trona		.46894		Na_2CO_3
Trona		.37167		$NaHCO_3$
Trona		.15939		H_2O
Trona		.2965		Ignition Loss
Trona		,7034		Na_2CO_3 Equivalent
Trona		.1991		H_2O
Trona		.0974		CO_2
$NaHCO_3$		.36895		Na_2O
$NaHCO_3$		2.6905		Trona
$NaHCO_3$		.3691		$H_2O + CO_2$
$NaHCO_3$		.6309		Na_2CO_3 Equivalent

Appendix 4 — Some definitions for statistical evaluations

Standard deviation, s; individual result, x. ; mean value, x ; number of results, n; true value, μ and student's t value have their common meanings. Student's t can be calculated as follows, where t_{table} is a table value at a given confidence level.

$$t_{calculated} = \frac{|\mu - \bar{x}|\sqrt{n}}{s}$$

$$R = \frac{\text{calculated}}{t_{table}}$$

A value of R which is larger than 1.0 indicates systematic error for a set of results. A confidence level of 95 % has been employed in this study.

4. X-ray diffraction spectrometry. — Finely powdered sample is rotated in front of X-ray beam to allow the formation of Bragg angles critical for all the crystal layers. The layers corresponding to these angles cause constructive interference of source radiation; and high intensity of source beam thus formed is detected by diffractometer to form convenient spectra. These spectra are further evaluated and by d values of (hkl) surfaces, mineral composition of sample is determined by the aid of ASTM data cards.

RESULTS

The studies were carried out to adopt standard methods for the analysis of trona samples, considering the interferences arising from silicates and other minerals present in trona samples. Among the methods in literature for the speciation of $NaHCO_3$-Na_2CO_3 in trona samples, the most applicable ones are $BaCl_2$ titration, $AgNO_3$ external indicator, and potentiometric titration. These three methods were tried on synthetic Na_2CO_3-$NaHCO_3$ mixtures for comparisons of analytical performances. Typical results are given in Table 1 for a synthetic sample. Total alkalinity values given in Table 1 and in other results were determined by potentiometric titration method. The errors found in Na_2CO_3-$NaHCO_3$ speciation by potentiometric method were higher then other methods. In order to further investigate this, a synthetic solution containing Na_2CO_3 only was analyzed by potentiometric titration method and Na_2CO_3 percentage was found as 106±1 from the first end point and 100±1 from the second end point. These predeterminations demonstrated that total alkalinity determined by potentiometric titration were correct but speciations were not correct. Seven trona samples obtained from Beypazarı were analyzed using $AgNO_3$ external indicator, $BaCl_2$ titration and potentiometric titration for the comparison of Na_2CO_3-$NaHCO_3$ speciation and the selection of a simple routine method for this analytical problem (Table 2). In these samples, the values of total alkalinity by potentiometric titration, trona percentages, XRDS results and results by other methods were also given (Table 3). The results of analyses were compared with theoretical trona values by student's t test; where the total alkalinity results are taken as basis for the theoretical values. 95 % confidence level, which is commonly used by analytical chemists, was employed as the basis of evaluation. The results of analytical determinations of seven trona samples were compared to theoretical results. At 95 % confidence level, R values of trona samples from Beypazarı for the percentages of Na_2CO_3 are 0.008 in $BaCl_2$ method, 3.25 for $AgNO_3$ external indicator method and 3.26 for potentiometric method; for the percentages of $NaHCO_3$ the same values are 0.59 for $BaCl_2$ method, 2.83 for $AgNO_3$ external indicator method and 3.59 for potentiometric method, systematic error is indicated when R>1. The results of $BaCl_2$ method show that this method gives the results which are closest to the theoretical values; compared to the other methods.

Table 1 - Representative results for synthetic trona sample
True values; 33.3 % $NaHCO_3$, 66.6 % Na_2CO_3

Method	*% Value found, ($\overline{X}$ ± S)*	
	$NaHCO_3$	*Na_2CO_3*
Potentiometry	29.0∓1.0	71.0∓1.0
$AgNO_3$	33.0∓0.5	67.1∓0.5
$BaCl_2$	34.0∓0.5	66.0∓0.5

Table 2 - Detailed analytical results for Beypazarı trona samples

Sample no.	*Total alkalinity (%)*	*Trona (%)*	*Water insoluble part (%)*	*SO_4 (µg/g)*	*Cl (µg/g)*	*Ca + Mg (µg/g)*	*Diognastic result by XRD*
06.16A.1A	69.17	98.33	0.44	<100	<100	<100	Trona, brugnatellite
06.16A.2A	55.28	78.59	20.44	<100	<100	<100	Trona, dolomite
06.23.1A	68.77	97.77	1.06	<100	<100	<100	Trona
06.21.1	68.77	97.77	1.37	<100	<100	<100	Trona
06.21.2	67.30	95.68	2.75	<100	<100	<100	Trona
06.23.2A	13.35		80.67	<100	<100	<100	Dolomite, quvars, analcite, feldspar, natron
06.21.3	68.77	97.77	1.11	<100	<100	<100	Trona, brugnatellite

Table 3 - Comparison of the results for Na_2CO_3 and $NaHCO_3$ content in Beypazarı trona samples by different methods

Sample no.	*Na_2CO_3 % by the method indicated*				*$NaHCO_3$ % by the method indicated*			
	$BaCl_2$	*$AgNO_3$*	*Potentiometric*	*Theoretical*[a]	*$BaCl_2$*	*$AgNO_3$*	*Potentiometric*	*Theoretical*
06.16A.1A	45.76	46.90	50.79	46.04	37.10	35.30	31.00	36.47
06.16A.2A	37.08	37.28	40.74	36.80	28.84	28.53	24.10	29.15
06.23.1A	45.73	46.63	51.32	45.78	36.54	35.12	30.60	36.26
06.21.1	45.68	46.24	48.68	45.78	36.61	35.72	32.30	36.26
06.21.2	44.82	45.50	50.26	44.80	35.63	34.56	28.07	35.49
06.21.3	45.90	46.84	48.15	45.78	32.26	34.77	33.11	36.26

a Theoretical values as calculated from total alkalinity results (Appendix 1).

As it was mentioned in «Introduction», some studies were done to investigate the possible interferences in analysis by clays and other chemicals present in trona mineral.

The impurities were predetermined by XRD spectrometry, and analyses were modified according to the interferences thus known. In order to decide on modifications, following studies were done on potentiometric titration method which is capable of giving results rapidly.

Interference of clays: In order to verify the interferences of clay minerals on carbonate-bicarbonate end points, seperate titration curves were drawn for the mixtures of i) Na_2CO_3, clay and water and, ii) Na_2CO_3 and water As it is shown in Figure 2, the presence of clays has no effect on carbonate-bicarbonate end point. The mixtures were prepared as described in «experimental». This procedure involves leaving the solution overnight, thus allowing effective sedimentation of clay. When the solutions were titrated without waiting overnight, titration curves ambiguous and irreproducible end points.

Interference of dolomite: Possible interference of dolomite was also investigated, titration curves were drawn for the cases of i) Na_2CO_3, dolomite and water; ii) dolomite and water unfiltered mixture; iii) dolomite and water, filtered mixture. The results are shown in Figure 3. It has been observed that carbonate-bicarbonate end point was affected when dolomite containing sample was not filtered. In this case, during the course of titration, as pH is lowered after the first end point probably a part of dolomite gradually is dissolved causing a higher content of bicarbonate ion. Consequently, second end point is delayed.

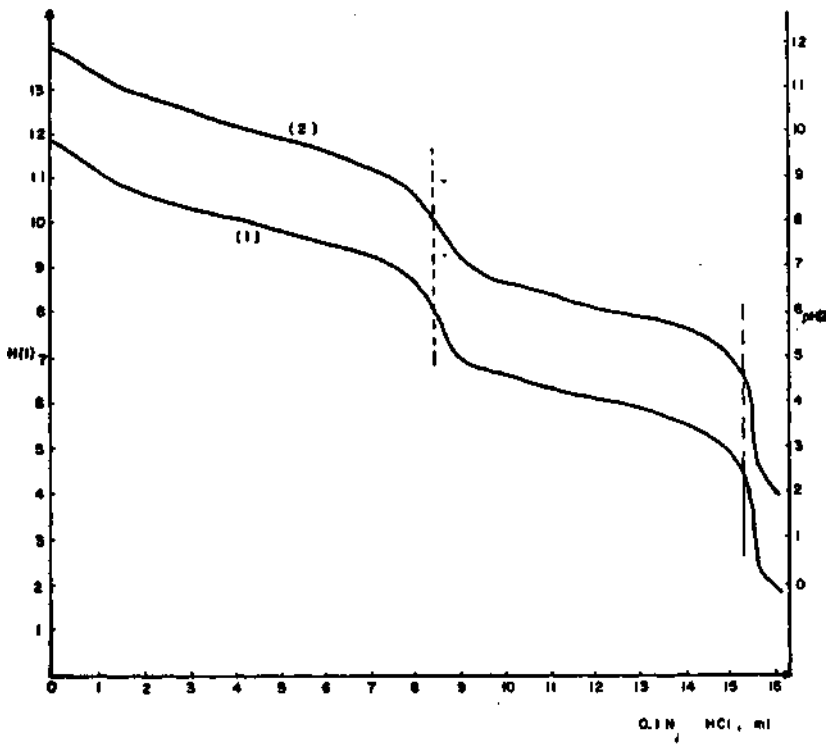

Fig. 2 - The effect of clay minerals on potentiometric titration of Na_2CO_3.
(1) 1.0 g Na_2CO_3 + 0.5 g clay + 100 ml distilled water (pH (1) scale);
(2) 1.0 g Na_2CO_3 + 100 ml distilled water (pH (2) scale).

In Figure 4, titration curves for a natural trona solution containing dolomite are shown. When solution was left for 3 hours, titration of aliquot taken from the clear part of the mixture gave end points corresponding to Na_2CO_3 content only. On the other hand a stirred mixture gave erroneous end points because of interference effects by dolomite which is gradually dissolved by addition of titrant, HC1.

According to the statistical evaluation, $BaCl_2$ titration method is the best approach for carbonate-bicarbonate speciation. This method was applied on 5 duplicates of a trona sample. Results and statistical evaluation are given in Table 4. Compared to the theoretical values, results involve errors of 0.4 % and 0.6 % for Na_2CO_3 and $NaHCO_3$, respectively. The same trona sample's XRD spectrum is given in Figure 5. This sample contains 95 % trona where XRD and other analytical results are consistent.

Although $BaCl_2$ method provides the best analytical results, potentiometric titration method is faster and more widely used. In the latter method, predetermined pH values of 8.30 and 4.5 are used for end points. However, in the working conditions, 8.30 for the first end point does not give accurate results as mentioned before. In order to find an empirical value for the first end point, 20 trona samples were analyzed by using total alkalinity and $BaCl_2$ titration results as well. First end point pH values to give accurate results, varied between 8.60 to 8.85 with an average value of 8.70 and a standard deviation of 0.07. Therefore, 8.70±0.07 and 4.5 have been suggested as empirical pH values for predetermined end points.

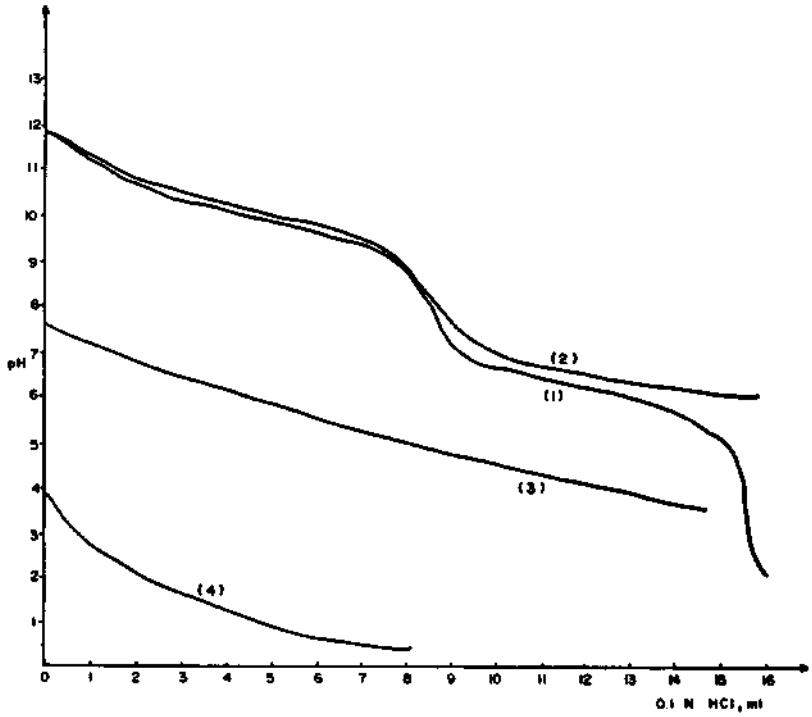

Fig. 3 - The effect of dolomite on potentiometric titration of Na_2CO_3. (1) 1.0 g. Na_2CO_3 + 100 ml distilled water; (2) 1.0 g. Na_2CO_3 + 0.5 g dolomite + 100 ml distilled water. The mixture was not filtered or left to stand for sedimentation; (3) 0.5 g dolomite + 100 ml distilled water, unfiltered; (4) 0.5 g dolomite + 100 ml distilled water, filtered.

Table 4 - Results obtained by $BaCl_2$ titration and theoretical methods for a trona sample

	Total alkalinity	*$BaCl_2$ titration*		*Theoretical*	
	Na_2O%	*Na_2CO_3%*	*$NaHCO_3$%*	*Na_2CO_3%*	*$NaHCO_3$%*
1	39.14	44.36	35.81	44.61	35.36
2	39.14	44.43	35.70	44.61	35.36
3	39.22	44.42	35.91	44.70	35.43
4	39.45	44.42	35.91	44.97	35.64
5	39.30	45.08	35.07	44.79	35.50
$\bar{X}$	39.25	44.54	35.68	44.74	35.46
s	0.13	0.30	0.35	0.15	0.12

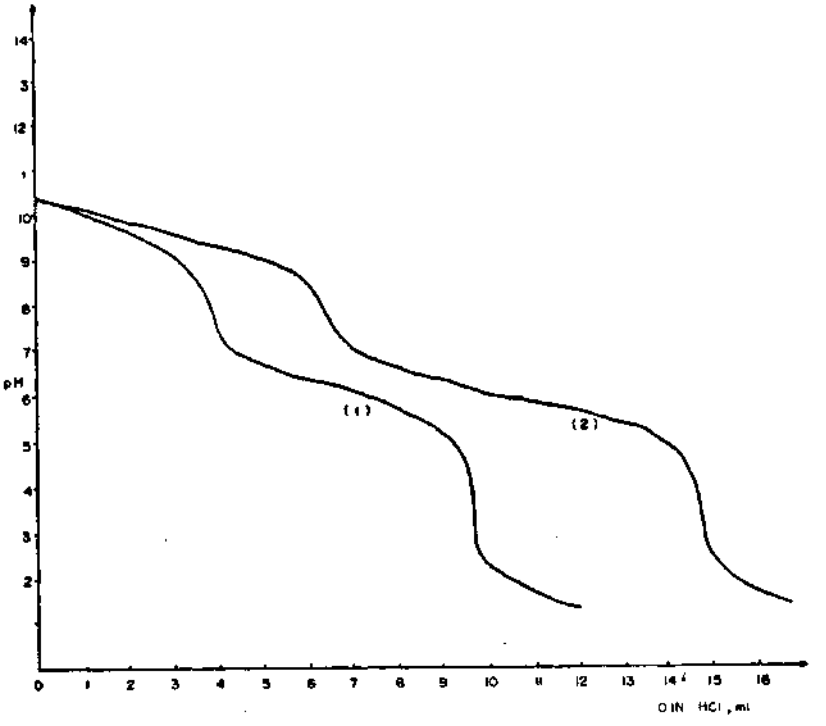

Fig. 4 - The interference of dolomite on potentiometric titration of trona samples.
Sample : 10.0 g / 500 ml dolomite
(1) Titration of clear solution after waiting for 3 hours for sedimentation;
(2) The titration of the mixture as in (1) after being stirred.

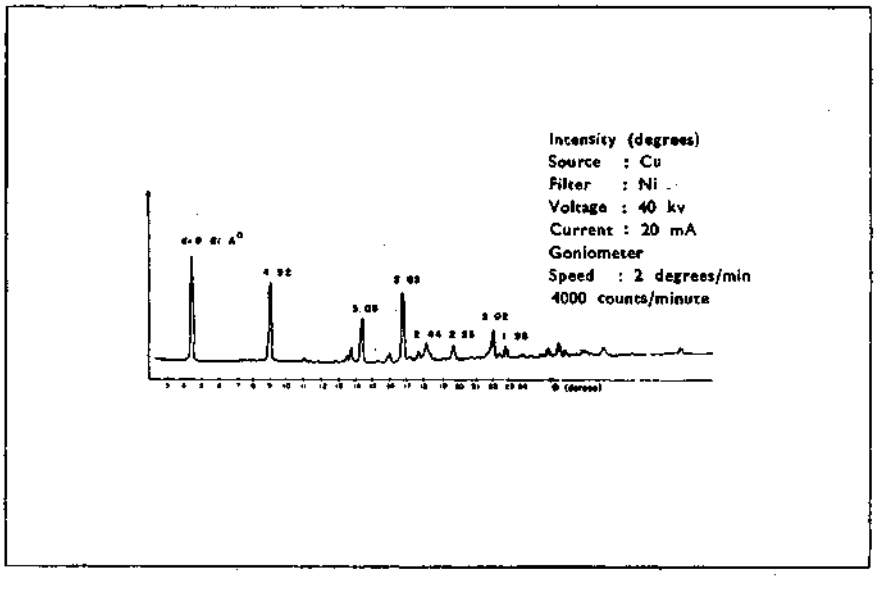

Fig. 5 - X-ray diffraction spectrum of a trona sample.

DISCUSSION

It can be concluded that for rapid trona analyses, potentiometric titrations using corrected pH values as predetermined end points, can both provide accurate results and give total alkalinity and Na_2CO_3 percentages in one step process. On the other hand, $BaCl_2$ titration method can provide results more accurate than those by potentiometry; but for total alkalinity values still another method is required. Therefore $BaCl_2$ method is a longer method with consequently higher expenses. In this study, the quality of the analytical performance by potentiometry has been improved. The difference between the theoretical and empirical end point values, however, could not be explained at this stage.

In addition, the results of this study suggest that major impurities in a trona sample should be qualitatively predetermined by XRD Spectrometry and necessary precautions for possible interferants thus can be taken.

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