

**Microdetermination of Barium in Formation Water By
Atomic Absorption Spectrophotometry
Using Matrix Matching Procedure**

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Summary: An improved method is described for the determination of barium occurring at trace levels in water associated with oil deposits in natural formation water. Better results were obtained by using matrix matching procedure than the standard addition method. Effect of high concentrations of calcium, strontium, potassium and sodium on barium absorbance have also been investigated.

Introduction

Formation water, the water present alongwith crude oil in oil reservoirs normally contains high concentrations of alkali and alkaline earth metals. Sea water is usually injected in oil beds to pressurize the crude oil for its recovery [1]. Sea water contains a large quantity of sulphate ions and on mixing with formation water insoluble alkaline earth sulphates are formed which are deposited in pipelines as a hard scale [2], and ultimately blocks them. The scale formed by calcium and strontium ions is relatively easier to remove as compared to the hard barium sulphate. In order to deal with the scale problem an accurate knowledge of calcium, strontium and barium concentrations in formation water is very essential [3]. Calcium and strontium ions are usually present in larger amounts so their determination does not involve any difficulty. However, problems are encountered in barium determination from formation water, owing to its relatively smaller amount.

Flame emission and atomic absorption spectrophotometry, using standard addition procedure in normally employed for complex matrices [4]. Unfortunately, this technique failed in this case because the interference effect varies with the ratio of the interfering element to barium [6], resulting in a non-linear graph. To achieve the desired accuracy, a matrix matching procedure is thus developed in the present studies. Though a rough idea of the major constituents of formation water is essential but the result, obtained by this procedure were much better than those obtained by standard addition method. Accuracy of the results was reasonable when compared with those achieved by spectroscopic method [7].

Experimental

Equipment:

A Perkin-Elmer Model-305, Atomic Absorption Spectrophotometer equipped with a servoscribe chart recorder

and standard barium hollow cathode lamp was used. Absorption of barium was measured at 553.4 nm.

Reagents:

All reagents used were of Analar Grade. Doubly distilled water was used through out the studies.

Solutions of barium (0.1M) strontium (0.1M) and calcium (0.1M) were prepared from their anhydrous carbonates, by dissolving their appropriate amounts in a minimum quantity of 6M hydrochloric acid and then diluting with water. Sodium (2M) and potassium (0.1M) stock solutions were prepared by dissolving their Chlorides whereas magnesium ribbon was treated with 6M hydrochloric acid to prepare (0.1M) solution of magnesium.

To check the accuracy of the proposed procedure, a synthetic sample of formation water was prepared on the basis of the approximate composition of Forties Formation water [8]. The concentration of different components in the final solution was; barium (0.002M), strontium (0.007M) calcium (0.08M) magnesium (0.015M) potassium (0.01M) and sodium (1.3M).

Natural sample of formation water was provided by the B.P. (British Petroleum) Ltd.

Procedure:

Aliquots of 0.01M barium solution (0.5-2.5ml) were transferred into five 100ml calibrated flasks. To each flask 8 ml of calcium and 6.5 ml of sodium solutions were added. 10 ml of 10% hydrochloric acid were added and contents were diluted to the mark with water. A blank was prepared by adding appropriate quantities of the reagents except barium solution. The solutions were aspirated in a medium

air-acetylene flame and absorbance of each solution was measured against the blank.

Synthetic and natural samples were diluted ten times with a 1% hydrochloric acid content in the final volume.

Results and Discussion

A linear calibration graph in the range $0.5-2.5 \times 10^{-4}$ M barium was obtained with a significant intercept along Y-axis (Fig.1). The intercept was probably due to the high concentrations of sodium and calcium ions present in the standards as well as in blank. The results of natural formation water samples obtained by the described procedure (matrix matching) have been compared with those obtained by standard addition method and spectrophotometric method [7]. As shown in Table-1, standard deviation of the proposed procedure is far better than standard addition procedure and reasonably near to the values for spectrophotometric method.

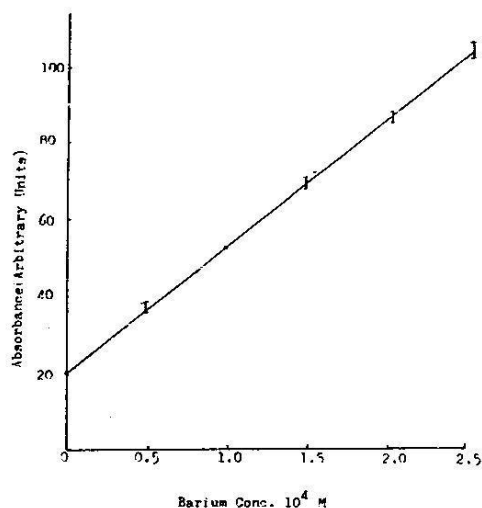


Fig-1: Calibration line for barium absorbance in the presence of sodium (0.13M) and calcium (0.008M) ions.

Table-1: Determination of barium from natural formation water by different methods.

Proposed method	Spectrophotometric Method	St. Addition Method
(Ba) = $X \times 10^{-3} M$	(Ba) = $X \times 10^{-3} M$	(Ba) = $X \times 10^{-3} M$
1.90	1.86	1.80
1.84	1.82	2.06
1.86	1.84	2.08
1.80	1.84	1.90
1.86	1.81	2.00
R.S.D. 2.0%	1.0%	4.9%

Effect of Matrix Ions:

The approximate concentrations of the common ions found in formation water are given in Table-2. The effect of these ions on barium absorption was studied both individually and also in the presence of each other. The concentration of interferent was varied from zero (0) to the maximum approximate concentration, keeping barium concentration to $2.0 \times 10^{-4} M$ level. The results illustrated in Table-3 revealed that maximum effect on barium absorbance was observed due to calcium and sodium ions, partially because of their high concentration and partially due to their behaviour as ionization buffers. The enhancement effect of calcium on barium absorbance decreased markedly, in the presence of sodium ions. Effect of other ions is very slight and becomes negligible when noted in the presence of sodium and calcium ions. Hence, the only constituents required to be added in the standards, as well as in blank are the sodium and calcium ions, for the purpose of matrix matching.

Table-2: Approximate Composition of Forties Formation water [8].

Ions Present	Concentration
Na ⁺	1.3M
K ⁺	0.01M
Mg ⁺⁺	0.015 M
Ca ⁺⁺	0.08 M
Sr ⁺⁺	0.007M
Ba ⁺⁺	0.002M

Table-3: Interference Effect of Matrix Ions.

Ions	Concentration	Rel. Error in Barium Abs.
Na ⁺	0.13	+ 18%
K ⁺	10^{-3}	+1.5
Mg ⁺⁺	1.5×10^{-3}	0.0
Ca ⁺⁺	8.0×10^{-3}	+20.0
Sr ⁺⁺	7.0×10^{-4}	-0.3
Cl	0.14M	+1.0

Effect of Variation in Calcium and Sodium amount:

A 5% variation in the concentration of calcium and sodium had almost negligible effect on the absorbance of barium. In the plot of absorbance VS variation in the calcium and sodium contents of formation water the absorbance remains almost unaffected, thus the preliminary analysis of formation water is not a very critical step.

Effect of Releasing Agent:

Releasing agents have been commonly employed in atomic absorption spectroscopy to remove chemical interferences, especially in the determination of alkaline earth metals [9]. These reagent generally had been added directly in excess, to the solution to be determined. In the present studies varied concentrations of lanthanum had no significant effect on the absorbance of barium ions especially in the presence of calcium and sodium ions. Because the sodium ions were present in large excess and themselves acted as releasing agents, so the need of an extra releasing agent was eliminated.

Comparison with the standard addition procedure [4,5]:

Results of barium determined in synthetic samples by the proposed method, were compared with those obtained by standard addition method, using the following aprocedure.

"Aliquots of barium solution (0.5-2.5 ml) were added in five 100ml flasks. Now added 10 ml of synthetic samples and 10 ml of 10% hydrochloric acid. Five different sets of the standards were prepared. Blanks were prepared without barium ion. The solutions were aspirated to air-acetylene flame and the absorbance was plotted against the concentration of analyte added. The concentration of barium in sample was achieved by extrapolation."

The results obtained by standard addition procedure had a poor precision than those achieved by the proposed procedure (Table-4).

Conclusion

High accuracy and precision is required in barium determination from formation water. Standard addition

Table-4:
Determination of barium from synthetic formation water samples (barium present= 2×10^{-3}).

Proposed Method		St. Addition Method	
Barium Found (10^{-3} M)	%age recovery	Barium Found (10^{-3} M)	%age recovery
1.98	99	1.80	90
2.00	100	2.06	103
2.06	103	2.08	104
1.94	97	1.90	95
2.04	102	2.00	100
RSD	± 2.3%	RSD	± 5.76

procedure, using atomic absorption spectroscopy does not give the desired response, so a matrix matching procedure was developed, which gave reasonably acceptable values. The only complication with the proposed method is that a prior knowledge of the approximate concentration of various constituents is necessary. The effect of various parameters was studied on barium determination.

The proposed procedure can be effectively used for different geological material when barium is present, in the high concentration of calcium and other interfering ions. The method is simple and reliable without involving the complicated steps of separation or complexation as in the case of spectroscopic measurement.

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