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# Analysis of Barium in Barium Sulfate and Diagnostic Meals Containing Barium Sulfate Using Atomic Absorption Spectroscopy

**R. A. SHARP* and A. M. KNEVEL**

**Abstract** □ An analytical method was developed for the determination of barium in barium sulfate and diagnostic meals containing barium sulfate using atomic absorption spectroscopy. The procedure provides satisfactory levels of accuracy and precision and overcomes many disadvantages of currently used procedures such as lack of barium specificity, lengthy analysis time, and interference by diagnostic meal additives.

**Keyphrases** □ Barium—determination □ Diagnostic meals, barium sulfate—barium determination □ Atomic absorption spectroscopy—analysis

Barium sulfate has been the medium of choice for roentgenographic examination of the gastrointestinal tract for over half a century. In spite of its long use, an assay procedure was not included in the USP until publication of the 18th revision. Major drawbacks that contribute singly or collectively to the shortcomings of existing methods of barium sulfate analysis include lack of accuracy, lack of precision, excessive cost, and lengthy analysis time.

Several analytical techniques have been developed for barium analysis. These include: complexometric procedures using ethylenediaminetetraacetic acid (EDTA) as the titrant (1, 2), flame emission spectroscopy (3), X-ray (4), anodic arc excitation spectrography (5), gravimetry (6–8), and turbidimetry (9, 10). A gravimetric method based on fusion of the sample with sodium carbonate followed by precipitation of barium as barium chromate is the official assay procedure found in USP XVIII (11).

The introduction of atomic absorption spectroscopy (AAS) as a new analytical tool offers another approach for the assay of barium sulfate. The method is very sensitive and highly specific for barium ion (12). Roe *et al.* (13) reported a method for the estimation of low concentrations of sulfur and sulfate in biological materials by conversion of sulfate to barium sulfate and subsequent barium determination by AAS. The objective of this investigation is to evaluate atomic absorption spectroscopy as a method for barium content determination of barium sulfate and diagnostic meals containing barium sulfate.

## EXPERIMENTAL

**Equipment**—A Perkin-Elmer model 290 atomic absorption spectrophotometer with a single slot, model 290-1169, burner head and a Perkin-Elmer Intensitron barium lamp were used for barium content determinations. A lamp current of 7 mamp. was used. The instrument slit width was set at 7 Å, and a meter damper setting of 3 was used. The instrument was adjusted to a coarse select element setting of approximately 709.7. Standard tanks of compressed air and acetylene were used with regulator settings of 40 and 8 psig., respectively. The instrument fuel flow was adjusted to approximately 14.1 and the air flow to approximately 14.8.

**Reagents**—The initial consideration in the development of an AAS method of analysis for barium sulfate was to find a solvent system in which barium sulfate would be readily soluble. This chemical is virtually insoluble in water and other solvents suitable for use in AAS (14, 15). Organic solvents, such as dimethyl sulfoxide and *N,N*-dimethylformamide, and aqueous solutions containing selected inorganic salts, such as zirconium nitrate and zirconium chloride, were evaluated experimentally and found to be unsuitable as solvent systems. In the course of the solubility study, ethylenediaminetetraacetic acid and its salts were also investigated. It was found that a 0.05 *M* disodium ethylenediaminetetraacetic acid ($Na_2EDTA$) solution USP XVIII, adjusted to pH 10 with 2 *N* sodium hydroxide solution had solubility properties suitable for the analytical procedure.

Because USP reference standard barium sulfate was not available for the preparation of a barium standard curve, barium sulfate USP was purified in the following manner. The material was dissolved in concentrated sulfuric acid, precipitated by dilution with distilled water, collected by vacuum filtration through a fritted-glass filter, dried, and finally ignited at 1000° for 4 hr. The process was repeated twice, and the purified barium sulfate was stored over silica gel. The barium chloride evaluated for standard curve samples was reagent grade containing 2 moles of water of crystallization. Lanthanum chloride was obtained from a commercial supply house and was of unknown grade. Barium sulfate USP and two commercial diagnostic meals containing barium sulfate were used in the evaluation study. The barium sulfate was obtained from a single lot and assayed following the USP XVIII gravimetric procedure with one exception. The barium sulfate and sodium carbonate mixture was fused using a muffle furnace instead of a blast burner. After the clear melt was obtained, it was then heated at 1000° for 30 min. The results of three determinations were 98.95, 99.92, and 100.0%. The two commercial sources of diagnostic meal were also obtained from single lots.

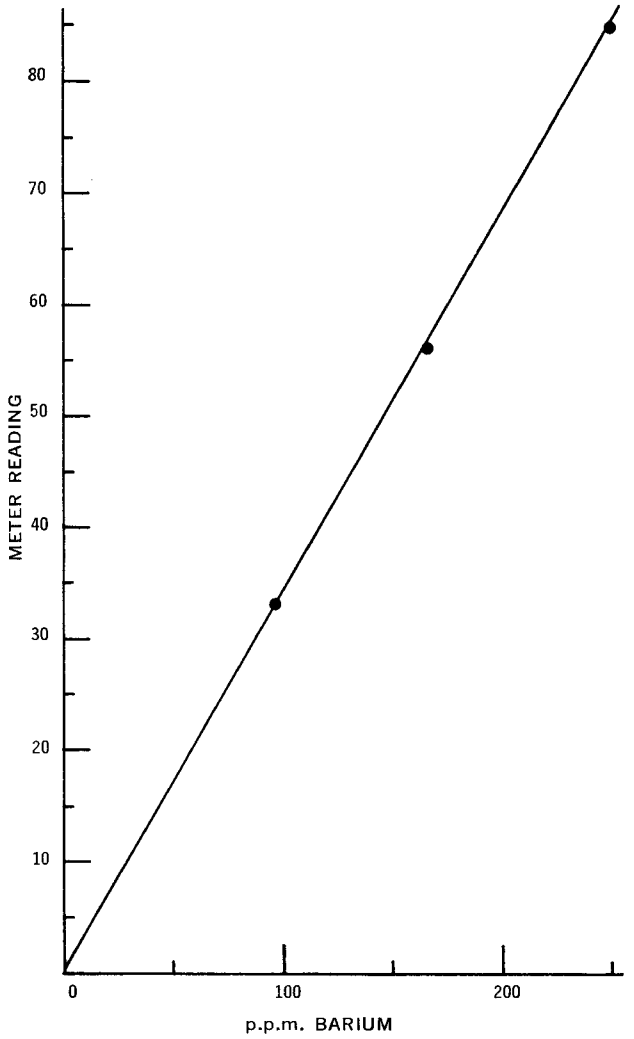


**Figure 1**—*Barium standard curve using barium sulfate in 0.05* M *$Na_2$ EDTA, pH 10.*

**Selection of Standard**—Water-soluble and water-insoluble barium salts were evaluated for construction of a standard barium curve. Aqueous solutions of barium chloride gave a nonlinear plot, and solutions of barium chloride in 0.05 *M* $Na_2EDTA$ (pH 10) gave excessive scatter. Both plots were unsatisfactory for barium determination. As shown in Fig. 1, a standard barium curve, prepared by dissolving purified barium sulfate USP in 0.05 *M* $Na_2EDTA$ (pH 10) solution, gave a linear plot. The reason for the unsuitability of barium chloride was not apparent but may have been caused by the presence of chloride ions.

The addition of lanthanum chloride was evaluated for the enhancement of barium absorption (13). This chemical did not significantly increase the barium response and therefore was not used in the final method.

**Sample Preparation**—Approximately 127 mg. of barium sulfate USP (150 p.p.m. barium) was mixed for 30 min. at 80° in 400 ml. of the solvent system (0.05 *M* $Na_2EDTA$, pH 10). The sample solution was cooled to room temperature and quantitatively transferred to a 500-ml. volumetric flask. The solvent system was added to volume, and the sample solution was thoroughly mixed. Diagnostic meal samples were prepared in a similar manner.

**Assay Procedure**—The atomic absorption spectrophotometer was allowed to warm up for approximately 1 hr. and adjusted for optimum response to a high concentration barium sulfate in the solvent system solution. Distilled water was used for zero adjustment. A standard barium curve was constructed from solutions of purified barium sulfate. Each sample solution containing barium sulfate was remixed by hand-shaking immediately prior to aspiration into the burner flame. Five individual instrument readings were made of each sample, and the average was used to calculate the barium content. Distilled water was aspirated between sample determinations to flush the system of residual sample. The burner head slot was cleaned by scraping with a razor blade after each five-sample determinations, and the nebulizer and pickup tube were cleaned after 10 sample determinations.

Ten individually weighed samples of barium sulfate USP and four individually weighed samples of each diagnostic meal were prepared and analyzed for barium content using AAS. To determine if meal components interfered with the assay method, studies were conducted using the meal formulations without barium sulfate under the same analytical conditions. Negligible absorbance (>0.02) was observed for both mixtures.

**Table I**—Results of Barium Sulfate USP[a] Assay

| Theoretical p.p.m. Barium | Experimental[b] p.p.m. Barium | Percent Recovery |
|---|---|---|
| 151.4 | 152 | 100.4 |
| 150.4 | 149 | 99.1 |
| 164.5 | 162 | 98.5 |
| 157.4 | 155 | 98.5 |
| 160.4 | 159 | 99.4 |
| 161.4 | 159 | 98.8 |
| 152.4 | 151 | 99.1 |
| 140.6 | 140 | 99.6 |
| 147.6 | 147 | 99.6 |
| 160.4 | 159 | 99.1 |
| | Mean | 99.2 |
| | Relative *SD* | 0.57 |

[a] 99.63% barium sulfate—average of three determinations. Assayed by USP XVIII modified method. [b] Calculated from average of five instrumental readings. Intrasample variations were all within ±1.0 p.p.m. barium.

## RESULTS AND DISCUSSION

Results of the assay of barium sulfate USP are shown in Table I. The mean percent recovery for 10 samples indicates good accuracy. Each determination was well within the limits of purity set forth in USP XVIII. The precision of the method, as shown by the relative standard deviation and the intersample variations, was also very good.

Table II shows the results obtained for the assay of the two diagnostic meals. Since the exact amount of barium sulfate in these samples is unknown, neither the mean percent recovery nor the standard deviation values are as significant as those of the known barium sulfate USP samples. However, the data do show that diagnostic meals can be assayed satisfactorily by AAS.

## CONCLUSIONS

A precise and accurate method of analysis was developed for barium sulfate using AAS. The procedure is particularly useful

**Table II**—Results of Diagnostic Meal Analysis for Barium Sulfate

| Labeled | Experimental[a] | Percent Recovery |
|---|---|---|
| | **Meal A, p.p.m. Barium** | |
| 152 | 153 | 100.6 |
| 156 | 160 | 102.5 |
| 153 | 153 | 100.0 |
| 146 | 148 | 102.0 |
| | Mean | 101.3 |
| | Relative *SD* | 1.16 |
| | **Meal B, p.p.m. Barium** | |
| 154 | 157 | 101.9 |
| 146 | 149 | 102.0 |
| 149 | 150 | 100.6 |
| 147 | 145 | 98.6 |
| | Mean | 100.8 |
| | Relative *SD* | 1.57 |

[a] Calculated from average of five instrumental readings. Intrasample variations were all within ±1.0 p.p.m. barium.

because it is applicable to the analysis of diagnostic meals containing barium sulfate.

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# Rapid Assay of Hydrogen Peroxide Solution (USP XVIII) *via* UV Spectrophotometry


**J. TIETJEN and A. MANCOTT**



**Abstract** □ Assay of hydrogen peroxide solution (USP XVIII) was accomplished by direct UV spectrophotometric analysis. This determination can be done in less than 30 sec. with a calibrated spectrophotometer and is comparable in accuracy to the USP XVIII titrometric procedure.



**Keyphrases** □ Hydrogen peroxide solution—analysis □ UV spectrophotometry—analysis


The spectrum and absorbance of hydrogen peroxide solutions in the UV range have been investigated (1–6). Bessun and Spitz (6) reported that dilute hydrogen peroxide solutions (10 mcg./ml.) followed Beer's law when measured at wavelengths between 195 and 220 nm. The molar absorptivity of hydrogen peroxide solutions decreases rapidly at wavelengths above 275 nm., and no appreciable absorbance is recorded at wavelengths greater than 375 nm.

To perform a direct UV spectrophotometric assay on 3% hydrogen peroxide solutions (USP XVIII) without employing time-consuming and less accurate dilution techniques, a wavelength of 304 nm. was chosen, which is substantially higher than that of maximum absorption. The very low molar absorptivity at 304 nm. permits direct measurement of hydrogen peroxide solutions in the 2.0–4.5% range.

The UV spectrophotometric assay reported here can be done in a matter of seconds with a calibrated spectrophotometer. It requires no chemicals or reagents and is comparable in accuracy to the USP XVIII titrometric procedure (7).

## EXPERIMENTAL

**Apparatus**—Spectra and absorbance measurements were made with a spectrophotometer[1]. Matched cells with a 1-cm. optical path were used.

**Reagents and Chemicals**—Hydrogen peroxide solution (30%)[2,3], 0.1 *N* potassium permanganate solution[4], and hydrogen peroxide solutions USP XVIII[5] were assayed. All other reagents used were of the highest commercial grade available.

**Procedure**—The spectrophotometer (slit width 5 Å, deuterium lamp) was adjusted to zero absorbance with distilled water. The wavelength was calibrated against a mercury emission spectrum and set at 304.0 nm. with the controls locked. Solutions of hydrogen peroxide were prepared by dilution of 30% hydrogen peroxide and standardized with 1.0 *N* potassium permanganate solution. Absorbances of the standard hydrogen peroxide solutions were measured. Samples of hydrogen peroxide solutions USP XVIII were assayed by measuring their absorbance at 304.0 nm. and comparing with the standards. The same samples were also assayed according to the USP XVIII titrometric procedure.

## RESULTS AND DISCUSSION

Absorbance readings for standardized hydrogen peroxide solutions in the concentration range of 2.1–4.3 g./100 ml. were obtained (Table I). A graph of concentration *versus* absorbance was linear, with a slope of 4.386. The concentration of hydrogen peroxide in a given sample is found from Eq. 1:

$$C = 4.386A \qquad \text{(Eq. 1)}$$

where $A$ = absorbance, and $C$ = grams of $H_2O_2$ per 100 ml. of solution.

[1] Bausch & Lomb, model 505.
[2] Fisher certified reagent.
[3] B&A reagent, Allied Chemical.
[4] Fisher certified reagent.
[5] Parke-Davis & Co., Detroit, Mich.