whenever the great excess of the main component interferes with other separation methods.

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Critical Parameters in the Barium Perchlorate/Thorin Titration of Sulfate

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The analysis for sulfur-containing species such as sulfur dioxide, sulfur trioxide, and sulfates in the atmosphere — both ambient and workplace — is an area of continuing and intense interest. The titrimetric determination of sulfate using barium perchlorate and the indicator Thorin (*1, 2*) has been recommended for the determination of sulfur dioxide (*3–6*), sulfur trioxide (*6*), and sulfuric acid (*7*). The original description of the method (*2*) recommends an apparent pH in the range of 2.5 to 4.0 and a nonaqueous solvent (alcohol) concentration of between 70 and 90% (v/v) for the titration, but little attention has been directed to the critical nature of these parameters in the analytical methods subsequently derived from this procedure (*3–7*). Indeed, one of the methods (*6*) does not even specify solution pH, although the titration has been reported to be sensitive to this factor (*1, 2, 8*). We report herein the results of an investigation of these parameters and the fact that careful control of both pH and solvent concentration is necessary for the accurate determination of the above mentioned sulfur species in the small samples encountered in industrial hygiene analyses. There is, however, a range of values for these parameters over which acceptable recoveries are obtained.

EXPERIMENTAL

For these experiments, a pH meter (Ionalyzer Model 801, Orion Research), with a standard glass pH electrode (Fisher Scientific Co., #13-629-1) and calomel reference electrode (Fisher Scientific Co., #13-639-52), were used to determine the apparent pH of the solutions titrated. "Apparent pH" is used (*2*) to denote the fact that the pH values for the alcohol solution are read directly from the meter, although the meter is standardized using aqueous pH standard solutions. The alcohol used in this study was that recommended in the industrial hygiene methods (*3–7*), 2-propanol (PrOH) (Fisher Scientific Company, ACS reagent grade). The pH was adjusted using 0.2 N $HClO_4$ (J. T. Baker Chemical Company, Analyzed Reagent); the volume used was ≤1 mL for these studies and did not alter the total volume significantly.

Titrations were performed according to standard procedures (*4, 7*) using a 2-mL microburet for the 0.005 M $Ba(ClO_4)_2$. The titrant was standardized by titrating to a visual end point 5.0 mL of 0.00403 N H_2SO_4 to which had been added 40.0 mL of PrOH and 3 drops of the indicator Thorin. Aliquots of standard sulfate solution (60 μg/mL, prepared from analytical reagent grade Na_2SO_4, J. T. Baker Chemical Company) were titrated after adjustment of solution pH and % PrOH to the desired values with a final volume of 50 mL. Two preliminary sets of titrations were run, using parameters based on the ranges suggested in the NIOSH Criteria Document (*4*). In the first set, the pH was held at 3.5 and the PrOH concentrations were varied from 60% to 100%. In the second set, the PrOH concentration was held constant at 85% v/v and the solution pH was varied over the range 2.0 to 8.0. For the data to be used for determination of the response surface, titrations were performed using 21 combinations of experimental factors covering the ranges of pH 2.0 to 4.6 and PrOH 60% to 95%. For each pH–% PrOH combination, the volumes of titrant used for sample and blank were recorded and a subjective evaluation was made of the visual end-point sharpness (1 = very diffuse, 2 = diffuse, etc., to 5 = very sharp). Duplicate titrations were run at eight combinations of the experimental factors which covered all of the end-point sharpness ratings. The magnitude of the RSD was inversely proportional to the sharpness ratings, and ranged from 0 to 5% with a mean value of 2.3%.

RESULTS AND DISCUSSION

In the preliminary titrations at pH 3.5, end points tended to be obscure and delayed at low (<80%) PrOH concentrations. At concentrations above 90% PrOH, the observed end points were grossly premature (Figure 1). The net effect is that low recoveries are obtained for solvent compositions below 70% PrOH and above 90% PrOH at pH 3.5. The problems with end-point determination were also evident in the substantially higher "blank" values obtained when titrations were run at pH ≤3.0 (Figure 2) or at PrOH concentrations ≤80% (Figure 1). These increases in "blank" values contribute to a decreased precision for analyses and effectively raise the lower concentration limit for the procedure. At low pH (e.g., pH ~3.0 at 85% PrOH or pH ~2.5 at 80% PrOH), titrant volumes tend to increase for both samples and blanks. Below pH 2.0 (at 85% PrOH), no end points were reached even with very large volumes of titrant (Figure 2). It has been shown previously that the titration is subject to interferences from "foreign" ions, including various cations (*1, 2, 8*) as well as anions (*1, 2*). This interference leads to a positive or negative bias which is related both to the species and relative concentration thereof. However, at low concentrations (*8*), a 20-fold excess of $NaNO_3$ produces only a small (<1%) error in the end point. The 2-fold excess of Na^+ at a concentration of 10^{-4} M used in this study should therefore have at most a very small effect. Accordingly, ion exchange was not used to remove the Na^+ prior to the titrations. Obviously, ion-exchange pretreatment should be considered in applications of the technique to field samples which might contain significant quantities of concomitant ions.

The data obtained in the last set of titrations were used for a response surface analysis, the object of which was to determine the range of combinations of pH and % PrOH which yielded acceptable (~100%) recoveries of sulfate ion. This analysis was carried out by using a weighted regression technique to determine the best mathematical model which fits an appropriate function of the independent variables, pH and % PrOH, to the dependent variable, fraction of sulfate recovered. The subjective evaluation of end-point sharpness was used as a statistical weight for the experimental observations because the observed recovery values were not equally reliable. Therefore, the more reliable values (values subject

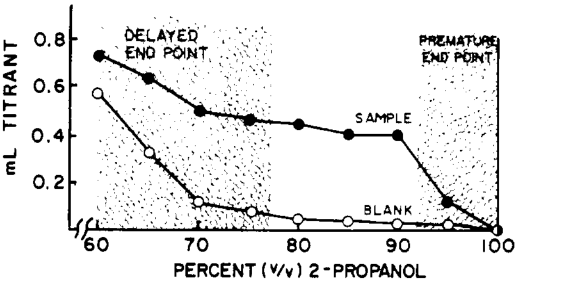

Figure 1. Volume of titrant (0.0053 M $Ba(ClO_4)_2$) required for sulfate (200 μg) sample and blank solutions as a function of PrOH concentration, at pH 3.5

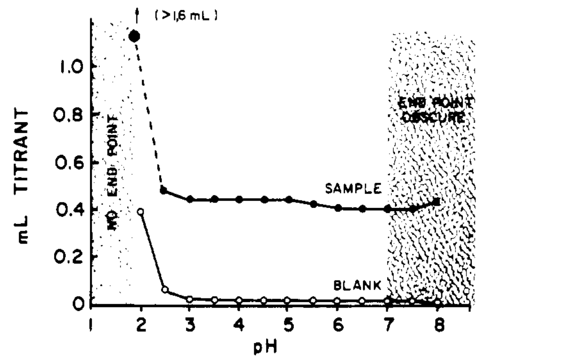

Figure 2. Volume of titrant (0.0053 M $Ba(ClO_4)_2$) required for sulfate (200 μg) sample and blank solutions as a function of pH at 85% PrOH

to less variance) which were associated with high values of end-point sharpness were given more weight in the analysis than those subject to greater variability. The end result is that the surface is forced to fit more closely to the more reliable values than to those more subject to error.

A fourth degree polynomial model was fitted to the data. Terms were removed in a stepwise manner, until every remaining term had an associated p-value of 0.15 or less. The final model selected was:

$$Y = -126.355 + 683.065\ X_2 + 30.324\ X_1X_2 - 1.3603\ X_1^2 - 1496.49\ X_2^2 + 1.500\ X_1^2X_2 - 53.726\ X_1X_2^2 + 1469.85\ X_2^3 - 528.635\ X_2^4 + 22.325\ X_1X_2^3$$

where Y = fraction of sulfate recovered, X_1 = pH, and X_2 = fraction PrOH. From this model, a contour plot was drawn to provide a "map" of the sulfate recovered as a function of the various combinations of pH and % PrOH (Figure 3). The contours shown correspond to predicted fractional recoveries of 0.6, 0.7, 0.8, 0.9, and 1.0. Anticipated recoveries would be optimal in the areas included within the 1.0 contours.

Shown superimposed on Figure 3 is a crosshatched area in which the end points were visually sharpest (end-point sharpness = 5). This information, used in conjunction with the results of the surface response analysis, indicates that optimum percent recovery and low variance would be obtained only in the region where the optima overlap. Thus, the experimental conditions recommended for titrations would include an apparent pH between 3.5 and 4.5 and a corresponding nonaqueous solvent concentration of 82–87% PrOH. These intervals constitute the largest rectangle fitting entirely within both the crosshatched area and the contour of predicted fractional recovery of 1.0. Other combinations of pH and PrOH concentration will also lead to acceptable recovery values but cannot be included if fixed, continuous intervals for these parameters are to be recommended. A broader pH range can be tolerated if the PrOH concentration range is limited; conversely, careful adjustment of pH allows more latitude in the PrOH concentration range. In the implementation of these titrations, the effects of dilution by the addition of the titrant and the aqueous acid solution used to adjust the pH must be taken into account to maintain the PrOH concentration in the optimum range. Also, the apparent

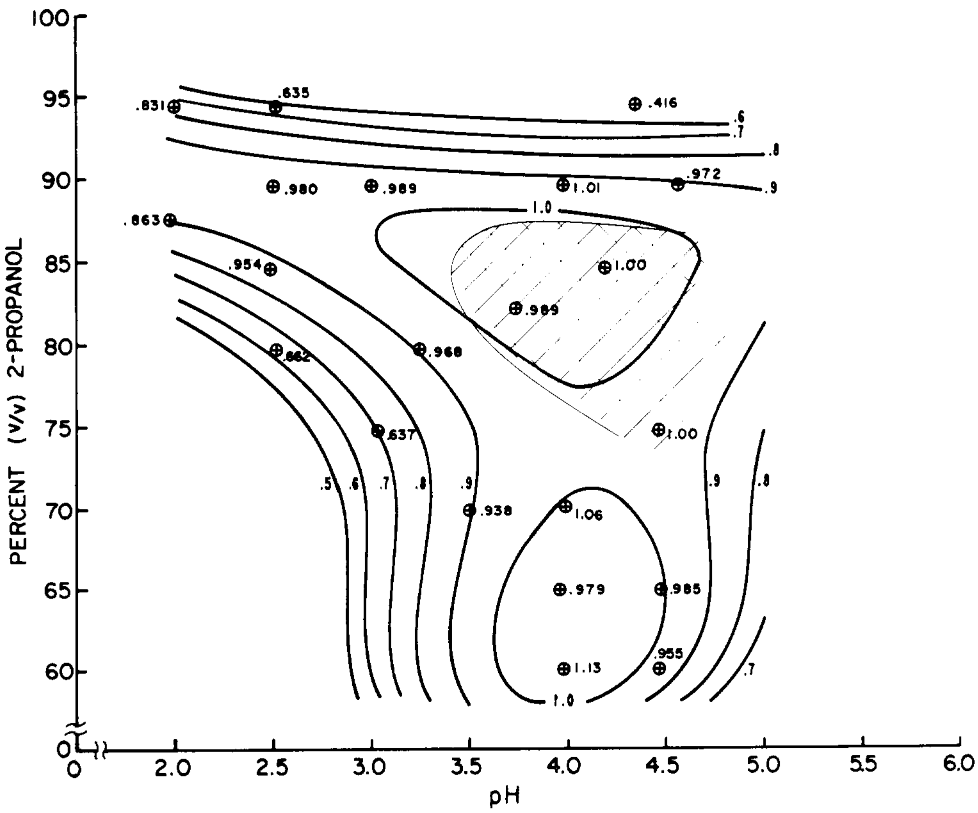

Figure 3. Fraction of sulfate recovered as a function of pH and % PrOH. Experimentally determined points are indicated by ⊕, with the corresponding fractional recovery. Cross-hatching indicates region of sharpest end points.

pH of the solution to be titrated must be carefully adjusted to be within the recommended range using a pH meter (not pH paper) for measurement.

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High-Speed Algorithm for Simplex Optimization Calculations

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In recent years the importance of optimization of experimental procedures and parameters affecting any given chemical analysis has been recognized. As a result, a number of workers have investigated the application of the sequential simplex method of Spendley and co-workers (*1*), as well as the later modifications by Nelder and Mead (*2*) to problems of chemical interest (*3–7*). Denton and co-workers derived the most recent modification of the simplex procedure for chemical applications and demonstrated its efficacy in optimization of the operation of a computer-controlled flame spectrophotometer (*8*). A number of studies of the application of simplex optimization methods to the development of weight vectors for chemical pattern recognition studies, primarily spectral data interpretation, have also been reported (*9–13*). In these latter studies, one of the major disadvantages of the technique has been the large amount of computer time required when high-dimensional problems are involved. For experiment optimization applications, computation time is often a secondary consideration, since problems frequently involve adjustment of only two or three operating parameters and their actual adjustment times may significantly exceed the computer time required to determine what the new settings should be. However, with the increasing advent of instruments capable of making rapid computer-controlled adjustment of a larger number of electronically controlled parameters, the need for more rapid simplex computation procedures may soon be felt even in experiment optimization applications. In the context of the previously-mentioned pattern recognition studies, the need for optimizing as many as 60 or more parameters, which are subsequently used in an automatic discriminant function for spectral analysis, makes the speed of the simplex algorithm employed a dominant factor in that application. Accordingly, a search for an even faster algorithm than those previously reported was initiated. We report here the successful outcome of that search.

DESCRIPTION OF THE HIGH-SPEED SIMPLEX ALGORITHM

Both the Modified Simplex method (*2*, *4*) and the Super Modified Simplex procedure (*8*, *9*) have been described in detail elsewhere as has their application to the problem of weight vector development for pattern recognition purposes (*9–13*). Therefore, only a brief summary of the fundamentals of the techniques will be given here to facilitate discussion of the improved algorithm. As originally defined (*1*), a simplex consists of a figure with $d + 1$ vertices located in a d dimensional space. Thus, in a two-dimensional space a simplex is a triangle, and in three-dimensional space, a tetrahedron. The coordinates of each vertex represent values of the d control variables, and the simplex algorithm provides a systematic procedure for exploring the experimental response obtained as a result of modifications in the control variables. By this means, if the simplex search is successful, an optimized response is ultimately obtained.

For pattern recognition, the simplex method was applied to the determination of the appropriate set of weights in a linear discriminant function which would produce an optimum response (defined as the maximum recognition of members of a training set of patterns which are classified with respect to some property of interest) (*9*). In order that the space searched be continuous, an additional response criterion (minimization of the perceptron (*14*) value) was combined with the recognition criterion. Subsequently, other response functions have been examined for that particular type of application (*13*).

Whatever protocol is used, the simplex optimization procedure involves searching for an optimum in response space by successively replacing the worst vertex of the simplex with better vertices. This is accomplished by reflecting the worst vertex through the centroid of the remaining vertices (CR). Therefore, the new vertex (W_{ki}^{new}) is simply a linear combination of the worst vertex and CR. As originally implemented for pattern recognition applications (*9*), the reflection procedure required complete recalculation of the value of CR on each iteration, using Equation 1.

$$CR_i = (1/(n-1)) \sum_{j \neq k}^{n} W_{ji} \qquad (1)$$

For the d dimensional space, n is equal to $d + 1$, the number of vertices of the simplex and the remaining vertices, j, are summed, excluding k, the vertex (weight vector) being replaced. Thus, each of the i coordinates of the centroid are calculated. This is unnecessary, since a running *overall centroid* (C) may be computed on each iteration by considering only the *changed* vertex (for pattern recognition, this is a weight vector). Equation 2 summarizes these relationships.

$$C_i^{new} = C_i^{old} + (1/n)(W_{ki}^{new} - W_{ki}^{old}) \qquad (2)$$

However, because the new summation, W_{ji}^{new}, changes from the old one only as a result of the changes in the vertex

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