least square method applying the following series of n equations:

$$\alpha_1 A_I(n) + \alpha_2 A_J(n) = A_L(n) \quad (22)$$

but assuming a three-phase system we applied n equations:

$$\alpha_1 A_I(n) + \alpha_2 A_J(n) + \alpha_3 A_K(n) = A_L(n) \quad (23)$$

where n is 80, because 40 sine and 40 cosine coefficients were used. I, J, K, and L are indices of samples included in particular combinations. For the two-phase criterion analysis, we considered 20, i.e., all the possible combinations of three from the six different samples, while in case of the three-phase criterion analysis, 15 combinations of four from the six different samples were included. For 18 combinations of the two-phase criterion analysis, R factors were bigger than zero. They varied from 0.08 to 0.29. In every case of the three-phase criterion (except for combinations 1 3 4 5, 1 3 4 6, and 1 2 5 6) R factor was zero, thus confirming that the system was really a three-phase one. The special case is represented by those combinations (1 2 5 and 1 3 4) of the two-phase criterion which give R factors zero, in spite of the system being a three-phase one (Table I). Such a paradoxical result arises either when the weight fractions of one phase in all the three considered samples are zero, or when the samples consist of pseudo-phases. Pseudo-phases are mixtures of two individual phases co-existing in the approximately same weight ratio in different samples. For example, in samples 1, 2, and 5 the weight ratio of phase 1 and phase 2 is constant and equal to 2:1. Such a mixture of two phases with constant weight ratio has a diffraction pattern which figures as an individual phase function for all the three samples mentioned. Therefore, the system including samples 1, 2, and 5 seems to be a two-phase one, i.e., to consist of a pseudo-phase X and of the individual phase 3. An analogous situation is obtained when combining samples 1, 3, and 4, but in this case we have pseudo-phase Y containing pure phases 2 and 3 of weight ratio 3:1. The presence of pseudo-phase Y and pure phase 1 in samples 1, 3, and 4 results in $R = 0$ in the two-phase criterion analysis, although the system is in fact a three-phase one. Such an incorrect conclusion is deduced only when all the samples included contain the same pseudo-phase. Pseudo-phases can be detected by comparing the R values for various combinations. For example, if samples 1, 2, and 5 and 1, 3, and 4 were to contain two phases only, the system consisting of samples 2, 3, and 5 would have been a two-phase one as well. However, the R value for the 2 3 5 combination was 0.24 showing that the system of the mentioned samples was in fact a pseudo-two-phase one. For the three-phase criterion including combination of samples 1 3 4 5, 1 3 4 6, and 1 2 5 6, and R-factors were higher than zero, because samples 1 3 4 and 1 2 5 represent pseudo-two-phase systems, which in combination with the other samples cause the appearance of the pseudo-four-phase systems. Thus the system of samples 1 2 5 6 seems to be a four-phase one, because it includes pseudo-phase X and pure phases 1 2 and 3. The two groups of samples 1 3 4 5 and 1 3 4 6 with the pseudo-phase Y and pure phases 1 2 and 3 represent another pseudo-four-phase system. After the permutation which replaces sample 5 by sample 1 or sample 6 by sample 1 in Equation 23, $\alpha_1 = 0$ was obtained by the least square method. $R = 0$ and $\alpha_1 = 0$ for the permutations mentioned, further confirm that samples 3 4 1 represent a pseudo-two-phase system. Therefore replacement of the constant $A_L(n)$ by term $A_I(n)$, $A_J(n)$ or $A_K(n)$ is recommended to avoid incorrect conclusion on the number of phases when pseudo-phases are present. The problem of pseudo-phases is of special importance in the study of some reaction mechanisms, where reaction products form simultaneously, at constant weight ratio. The theory of the criterion for the determination of the number of phases has already been applied successfully in the analysis of the calcium silicate hydrate system (*3*), portland cement clinker (*4*), and polyethylene–styrene co-polymer system (*5*).

LITERATURE CITED

(1) M. Teichgräber, *Faserforsch. Textiltech.*, **18**, 359 (1967).
(2) L. E. Copeland and R. M. Bragg, *Anal. Chem.*, **30**, 196 (1958).
(3) A. Bezjak and I. Jelenić, 2nd International Symposium on Autoclaved Calcium Silicate Building Materials, Hannover, 1969.
(4) A. Bezjak and I. Jelenić, Proceedings of the VI International Congress on the Chemistry of Cement, Moscow, 1974, in press.
(5) A. Bezjak, Z. Veksli, V. Tomašković, M. Bari, J. Dobo, and I. Dvornik, "Proceedings of the Third Tihany Symposium on Radiation Chemistry, Tihany, Hungary," 1971, p 1013.

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Titration Errors Inherent in Using Gran Plots

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Titration end points from a set of strong acid–strong base titrations were obtained with Gran plots and compared to visual indicator end points. The effects on titration error and end-point uncertainty which arise from measurement precision and the location on the titration curve of points used in making the Gran plots are discussed. Titration errors and end-point uncertainties comparable to visual indicator end points were obtained only by wisely selecting the points used in the analysis, carefully fitting the Gran plots to the points, and giving close attention to the precision of the measurements.

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In the past several years, interest has developed in using Gran plots to determine titration end points. Although this technique has been mentioned frequently in the literature and it is now beginning to appear in textbooks, little attention has been given to the titration errors which result from using it.

McCallum and Midgley (*1*) have discussed errors which originate in the chemistry of the particular titration reaction used and which cause non-linearities in Gran plots. For example, they describe a method to correct for the effects of the solubility of a precipitate in a precipitation titration, the autoprotolysis of water in an acid–base titration, and the effect of variation in activity coefficients. The authors make no statement, however, regarding the magni-

Table I. Titration Data

Titration of 100.00 ml of 0.01*N* HCl with 0.09956*N* NaOH

Trial 1		Trial 2		Trial 3	
ml Added	pH	ml Added	pH	ml Added	pH
0.00	2.07	0.00	2.01	0.00	2.01
1.00	2.11	1.00	2.10	1.00	2.10
2.00	2.18	2.00	2.17	2.00	2.15
3.00	2.23	3.00	2.21	3.00	2.20
4.00	2.30	4.00	2.30	4.00	2.30
5.00	2.39	5.00	2.38	5.00	2.39
6.00	2.50	6.00	2.49	6.00	2.50
7.00	2.61	7.00	2.60	7.00	2.61
8.00	2.80	8.00	2.80	8.00	2.80
9.00	3.18	9.00	3.17	9.00	3.19
10.00	end point	10.00	end point	10.00	end point
11.00	10.95	11.00	10.94	11.00	10.90
12.00	11.30	12.00	11.29	12.00	11.25
13.00	11.46	13.00	11.45	13.00	11.45
14.00	11.59	14.00	11.55	14.00	11.55
15.00	11.65	15.00	11.65	15.00	11.65
16.00	11.71	16.00	11.70	16.00	11.70
17.00	11.80	17.00	11.79	17.00	11.79

Trial 4		Trial 5		Trial 6	
ml Added	pH	ml Added	pH	ml Added	pH
0.00	2.05	0.00	2,18	0.00	2.14
1.00	2.10	1.00	2.24	1.00	2.20
2.00	2.18	2.00	2.30	2.00	2.30
3.00	2.24	3.00	2.37	3.00	2.39
4.00	2.30	4.00	2.41	4.00	2.45
5.00	2.39	5.00	2.50	5.00	2.51
6.00	2.50	6.00	2.60	6.00	2.61
7.00	2.61	7.00	2.74	7.00	2.73
8.00	2.70	8.00	2.92	8.00	2.90
9.00	3.20	9.00	3.29	9.00	3.22
10.00	end point	10.00	end point	10.05	end point
11.00	11.00	11.04	10.68	11.00	10.68
12.00	11.30	12.00	11.01	12.00	11.01
13.00	11.50	13.00	11.20	13.00	11.20
14.00	11.60	14.00	11.30	14.00	11.30
15.00	11.66	15.00	11.40	15.00	11.40
16.00	11.71	16.00	11.45	16.00	11.45
17.00	11.80	17.00	11.50	17.00	11.50

tude of titration errors resulting from using the Gran method compared to conventional end-point detector methods. In addition, no mention is made of errors arising primarily from the unique way in which the data are analyzed in a Gran analysis. These latter errors impose the most fundamental limitation on the method since, if they are unacceptable, poor results may be obtained from even the chemically least-complicated reactions. Neither the original work of Gran (*2*) nor his predecessor Sorensen (*3*) contained any discussion of errors inherent in the method now referred to as the Gran method or Gran plots.

Two advantages have been suggested (*4*) as favoring the use of Gran plots: 1) Fewer titration points need to be taken than with conventional methods, and 2) Measurements need not be made close to the equivalence point since this point may be obtained by extrapolation; therefore, problems associated with incompleteness of reaction or instability of measurements close to the end point can be avoided.

Recently we described the results of a theoretical study which evaluated titration errors associated with using Gran plots (*5*). This study suggested that the two previously mentioned advantages favoring Gran plots were significantly influenced by the number of data points chosen, the spacing between the points, the precision of the data, and constancy of the parameter 2.303 RT/nF. These conclusions relate directly to the errors arising from the way in which the data are analyzed but they are based only on theoretical titration data and the study considered only points taken before the end point. The present study uses experimental data to test the general conclusions of the theoretical work and considers various alternatives for analyzing data taken after as well as before the end point.

Table II. Gran Plot Titration Errors Related to the Number and Spacing of Data Points and to the Value of 2.303 RT/nF

Titration of 100.00 ml of 0.01*N* HCl with 0.09956*N* NaOH

Description of data	No. of points	Average titration error, %	Rel av dev, %	Av uncertainty at 95% C.L., %
Before the end point, no corrections	10	−1.76	1.44	8.69
	5[a]	−1.88	2.90	11.18
	5[b]	−1.51	0.47	6.43
	5[c]	−8.60	7.53	9.53
	3[d]	−1.20	0.73	5.23
	3[e]	−4.88	3.42	15.46
	3[f]	−20.19	9.38	9.38
Before the end point 2.303 RT/nF corrections	10	−0.58	1.01	7.59
	5[a]	−0.11	2.05	9.52
	5[b]	−1.68	1.03	5.66
	5[c]	−3.50	7.68	8.81
	3[d]	−2.27	0.91	1.52
	3[e]	−0.75	3.52	13.22
	3[f]	−20.30	10.74	9.11
After the end point, no corrections	7[g]	−1.45	0.91	6.61
	3[h]	−0.20	1.02	6.78
	3[i]	+1.49	0.42	2.08
After the end point, 2.303 RT/nF corrections	7[g]	−0.31	0.66	5.94
	3[h]	+0.79	0.54	4.51
	3[i]	+1.15	0.67	1.45

[a] Points at 0, 2, 4, 6, 8 ml. [b] Points at 1, 3, 5, 7, 9 ml. [c] Points at 0, 1, 2, 3, 4 ml. [d] Points at 2, 5, 9 ml. [e] Points at 0, 2, 6 ml. [f] Points at 0, 1, 2 ml. [g] Points at 11, 12, 13, 14, 15, 16, 17 ml. [h] Points at 11, 14, 17 ml. [i] Points at 11, 12, 13 ml.

The experimental conditions used for this study were chosen for several reasons: 1) Complications arising from the chemistry of the reaction are minimal; therefore, titration errors related to the way in which the data were analyzed could be highlighted. 2) The conditions were very nearly the same as those used to simulate titration data in the theoretical study as well as in the original work presented by Gran. 3) The large ratio of sample volume to titrant volume (10:1) minimized errors introduced by variations in activity coefficients due to dilution. 4) Accurate measurements of the end point could be made by conventional techniques and used as a reference to which the Gran technique could be compared.

EXPERIMENTAL

In the present study, six 100.00-ml samples of 0.01*N* HCl were titrated with 0.09956*N* NaOH. The titrant was delivered from a 10.00-ml microburet and the reaction medium was mixed with a Teflon bar magnet and a magnetic stirrer. A pH reading was made after each addition of 1.00 ml of titrant until a total of 17.00 ml had been added. The pH measurements were made with a Beckman general purpose glass electrode, a Fisher calomel electrode, and a Beckman "Zeromatic" pH meter which could be read with a precision of ±0.03 pH unit. Standard buffers of pH 3.00 and pH 7.00 were used to calibrate the meter. The calibration was only

performed once and it was not checked after each titration. In addition to the pH readings, a phenolphthalein end point was also recorded for each titration.

Gran plots of the titration data were made by performing a linear regression analysis on the following equation:

$$\left(\frac{100.00 + V}{100.00}\right)10^{(-pH \times K)} = K_1 V + [S]_0 \qquad (1)$$

where V is the volume of added titrant (ml), $(100.00 + V)/100.00$ is the correction factor for dilution of the sample by the titrant, $[S]_0$ is the initial concentration of sample, (moles/l), K_1 is the slope of the Gran plot, and K is a correction factor for the value 2.303 RT/nF. The linear regression analysis and all subsequent calculations were performed on a PDP-8/L minicomputer using FOCAL or a General Automation 18/30 computer using FORTRAN IV.

RESULTS

Table I shows the titration data recorded from the six titrations. A very slight drift in the pH meter calibration apparently occurred between Trial 4 and Trial 5. Data from Trials 5 and 6 were used as shown because no unusually deviant end-point errors were noted in the Gran analyses for these trials compared to Trials 1–4.

Table II shows the average titration error and precision obtained when Gran plots of the six titrations were made using data taken both before and after the equivalence point. The average titration error shown in the third column was computed by averaging the deviations of each Gran plot end point from its respective phenolphthalein end point. The fourth column shows the relative average deviation among the Gran plot end points. These values should be compared to a 0.18% relative average deviation among the six phenolphthalein end points. The fifth column shows the average end-point uncertainties at the 95% confidence limits. These limits were computed using parameters obtained from the linear regression analysis according to the method and formulas described by Bauer (*6*).

The data points selected for making the Gran plots used in compiling Table II were chosen to demonstrate how the location of the points on the titration curve and the spacing between these points affected the precision and accuracy of the titrations. Table II shows that the titration errors and uncertainty in locating the end point is reduced when a larger portion of the titration curve is represented both before and after the equivalence point.

Table II also shows the effect of varying the value of 2.303 RT/nF to find the best fit to a set of titration data. At 25 °C, the value of 2.303 RT/nF for the system studied is 59.16 mV and, during the course of a series of titrations, this value would not normally vary by more than ±5 mV. To find the value of 2.303 RT/nF giving the best fit of Equation 1 to a given set of titration data, K was assigned values ranging from 54.16/59.16 to 59.16/54.16 in increments of 0.2. A linear regression analysis was carried out for each value of K and the value of K giving rise to the largest regression coefficient was taken as the value providing the best fit to the data (*7*). Gran plots with 2.303 RT/nF corrections were made using this optimum value of K in Equation 1. Gran plots without this correction were made by setting $K = 1$. The results displayed in Table II show that, in six of the ten sets of titrations, significant improvement in both average titration error and average uncertainty at the 95% confidence level are achieved in end points determined from Gran plots made using corrected values of 2.303 RT/nF. The relative average deviation among the six trials is approximately the same and in all cases is larger than the 0.18% relative average deviation noted for the phenolphthalein end points. For the titrations in which the average titration error was not improved, the average uncertainty at the 95% confidence level was improved by using corrected values for 2.303 RT/nF. Additionally, in each of the four cases in which the titration error was not improved, one of the points taken closest to the end point was used—i.e., either 9 ml or 11 ml. When conventional titration curves were plotted using the experimental data and were compared to the theoretical titration curve for this titration, the experimental pH values at 9 ml and 11 ml consistently displayed some of the largest deviations (about 0.1 pH unit) from the theoretical values. This was because the pH was changing rapidly in this region and the readings were somewhat less stable. Consequently, when a sufficient number of other points were not used to compensate for this deviation, the best fit produced larger, rather than smaller, titration errors since all points were weighted equally.

Table III. Titration Errors Related to the Number and Spacing of Data Points and to the Value of 2.303 RT/nF When Two Gran Plots Intersect

Titration of 100.00 ml of 0.01*N* HCl with 0.09956*N* NaOH

Description of data	No. of points before the end point	No. of points after the end point	Average titration error, %	Rel av dev, %
No corrections	10	7	−1.60	0.41
	5[a]	3[f]	−1.12	0.57
	5[b]	3[f]	−1.38	1.16
	3[c]	3[f]	−2.90	1.62
	3[d]	3[f]	0.95	0.44
	3[e]	3[f]	−12.20	6.59
2.303 RT/nF corrections	10	7	−0.18	0.40
	5[a]	3[f]	−0.40	0.45
	5[b]	3[f]	+0.44	1.12
	3[c]	3[f]	−0.14	2.17
	3[d]	3[f]	−0.65	0.59
	3[e]	3[f]	−12.90	7.16

[a] Points at 1, 3, 5, 7, 9 ml. [b] Points at 0, 2, 4, 6, 8 ml. [c] Points at 0, 2, 6 ml. [d] Points at 2, 5, 9 ml. [e] Points at 0, 1, 2 ml. [f] Points at 11, 13, 17 ml.

Table III shows the results of determining the end points of the titrations by using the intersection of the pre-equivalence point and post-equivalence point Gran plots. Several conclusions may be drawn from Table III: 1) Smaller titration errors are obtained when the data points represent approximately 60% or more of the titration curve both before and after the equivalence point, and 2) Using values of 2.303 RT/nF corrected by the procedure described previously for Table II decreases the average titration error significantly but makes little change in the relative average deviation among trials.

An alternative method of determining Gran plot end points not evaluated in this study is to take several points just prior to the end point and several points immediately after the end point. Two problems associated with this approach are: 1) A prior knowledge of the approximate end point is required if only a small number of data points are to be collected, and 2) No problems such as incompleteness of reaction or instability of measurements near the end point must be associated with the system studied. Since one of the reasons mentioned previously for using Gran plots in the first place is to overcome at least the second of these limitations, this alternative method was not evaluated in the present study. In addition, as was pointed out earlier, the data points nearest the end point in this study frequently were some of the most unreliable points. Where

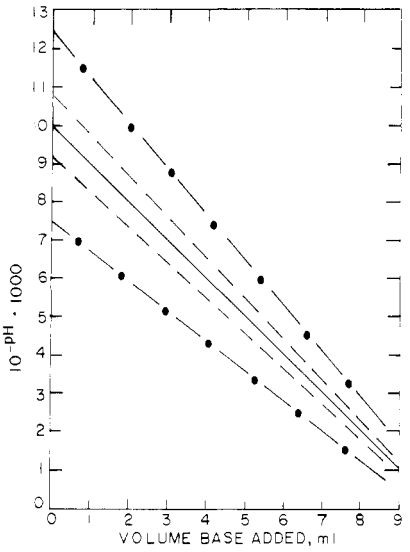

Figure 1. Gran plot error limits for the titration of 100.00 ml of 0.0100*N* strong acid with 0.1000*N* strong base

—— Theoretical; – – – ±0.03 pH units; – · – · ±0.10 pH units

the limitations do not apply, this alternative method would likely improve the results.

DISCUSSION

The data in both Table II and Table III indicate that the location on the titration curve of the points used in the Gran analysis greatly affects the titration error. For example, in an effort to keep from collecting points near the end point, because of incompleteness of reaction, etc., one should not choose points which all lie near the beginning or end of the titration curve. (For example, note the results obtained whenever points taken at 0, 1, and 2 ml were used.)

An important consideration in making Gran plots is the precision required in the measurements. It is important to observe that there is a direct relationship between concentration and the antilogarithm quantity plotted in a Gran plot but that there is a logarithmic relationship between the concentration and the quantity measured (pH or potential). In addition, the maximum error in reading the scale of a pH meter or millivoltmeter is normally constant over the entire scale range. The effect on a typical Gran plot of constant errors in reading a pH meter is shown in Figure 1.

The solid line in Figure 1 represents the values of $10^{-pH} \cdot 1000$ computed from the theoretical pH values which correspond to various volumes of added base. The estimated error in reading the pH meter, ±0.03 pH unit, was added to or subtracted from each of these theoretical pH values and then new values for $10^{-pH} \cdot 1000$ were computed to give points describing the lower and upper dashed lines. The lines represented by dots and dashes were computed in a similar manner except that a value of 0.1 pH unit was added to or subtracted from the theoretical pH at each point.

Figure 1 shows, for example, that a ±0.03 pH unit error in reading a low pH value has a much more profound effect on a Gran plot than does a ±0.03 pH unit error at a higher pH. Figure 1 also shows that even a normally acceptable precision in reading a pH meter (e.g., ±0.03 pH unit) can give rise to appreciable scatter in a Gran plot. Therefore, for the illustrative titration studied, if only pre-equivalence point data were used, the precision of the readings should be considerably better than ±0.03 pH unit in order to achieve titration errors comparable to those arising with conventional phenolphthalein end-point methods.

Table IV. Comparison of Methods Used to Construct Gran Plots

Description of data	Average absolute titration error, %[a]	Rel av dev, %
Both before and after end point, 2.303 RT/nF corrections	0.36	0.95
After end point, 2.303 RT/nF corrections	0.55	0.60
After end point, no corrections	0.82	0.97
Before end point, 2.303 RT/nF corrections	1.48	2.9
Before and after end point, no corrections	1.59	0.84
Before end point, no corrections	3.3	2.7

[a] Only trials using data representing 60% or more of titration curve were used.

Although the error lines in Figure 1 are not shown for post-equivalence point data, they continue to converge asymptotically on the theoretical line. This fact explains the smaller relative average deviations obtained with data taken after the end point as displayed in Table II.

The tendency toward negative titration errors shown in Table II and Table III is due, to a large extent, to the titration of small amounts of carbonate. Several additional titrations were performed under similar conditions to those represented by the data in Table I, but approximately ten points were recorded in the pH interval from 4 to 9. These data showed that the theoretical end point (pH 7.00) preceded the phenolphthalein end point by an average of 0.5% and a methyl red end point (pH 5.5) preceded the phenolphthalein end point by an average of 1.4%. Therefore, the data of Table II and Table III indicate that when points taken before the end point are used in the analysis, the Gran plot end points approximate the methyl red end point. When points taken after the end point are used, the Gran plot end point more nearly approximates the phenolphthalein end point. In both cases, the specific points selected have a very significant influence on the titration error attained. For example, the titration errors range from −0.31% to +1.15% even when the 2.303 RT/nF corrections are made on the points taken after the end point and even though the resulting end points do occur approximately 2% later in the titration than when only points taken prior to the end-point point are used.

In summary, the results of this study support the following conclusions regarding the use of Gran plots for determining the end point in the titration of a strong acid with a strong base. While the specific conclusions are directly applicable only to the system studied, they illustrate some of the factors which must be considered in determining the appropriateness of using Gran plots with any system.

1) Data points used in the Gran plot should represent as large a region of the titration curve as possible (approximately 60% or more in this study).

2) In general, pH or potential measurements must be made more accurately and precisely on high concentrations of the species measured than on low concentrations to minimize the error introduced when making a Gran plot.

3) Using points taken from regions of low hydrogen ion concentration (after the equivalence point in the titration

studied) provided the lowest titration errors and highest precision; however, only when the value of 2.303 RT/nF was selected to give the best fit to the data did the accuracy and precision approach that attainable using conventional phenolphthalein end points.

4) Table IV lists the various methods used to construct Gran plots in decreasing order of the absolute average titration error obtained with each. The values in Table IV were computed by averaging the values for each method presented in Tables II and III, disregarding signs and excluding trials in which points representing less than 60% of the titration curve were used.

The results of this study indicate that even for well-defined titration systems, of which the strong acid–strong base titration is representative, Gran plots must be used with caution if titration errors comparable to the conventional, visual indicator end-point detection techniques are desired. The two advantages suggested earlier which favor the use of Gran plots can be realized only by wisely selecting the points used, carefully fitting the Gran plots to the points (such as was done with the 2.303 RT/nF corrections in this study), giving close attention to the precision of the measurements, and accepting results which are at best slightly inferior to those attainable with conventional visual indicators.

LITERATURE CITED

(1) C. McCallum and D. Midgley, *Anal. Chim. Acta*, **65**, 155 (1973).
(2) G. Gran, *Analyst (London)*, **77**, 661 (1952).
(3) P. Sorensen, *Kem. Maanedsbl.*, **32**, 73, (1951).
(4) "Gran's Plots and Other Schemes", Newsletter of Orion Research Incorporated, **2**, 11 (1970).
(5) S. L. Burden and D. E. Euler, *Proc. Indiana Acad. Sci.*, **82**, 167 (1973).
(6) E. L. Bauer, "A Statistical Manual for Chemists", Academic Press, New York, NY, 1965, pp 85–92.
(7) J. D. Hinchen, "Practical Statistics for Chemical Research", Methuen and Co., Ltd., Great Britain, 1969, p 35.

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Solvent Extraction and Organic Carbon Determination in Atmospheric Particulate Matter: The Organic Extraction–Organic Carbon Analyzer (OE–OCA) Technique

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A method is presented for the determination of organic carbon in atmospheric aerosols. It consists of organic solvent extraction of samples collected on glass fiber filters followed by organic carbon analyzer analysis of the concentrated extracts as suspension in water. The organic solvent is removed in the vaporization zone (T = 100 °C) and the aerosol organic carbon is measured in the combustion zone (T = 850 °C) of an organic carbon analyzer. Twenty-six solvents and 24 binary mixtures were studied for their ability to extract aerosol organics. We define for this purpose the parameters EF (extraction efficiency) and OCEF (organic carbon extraction efficiency) with benzene as reference solvent. Nonpolar solvents have definite EF's and OCEF's, while polar solvents EF and OCEF vary with the ozone concentration (i.e., the smog chemical composition) observed during the sampling period. EF's correlate well with several solvent polarity parameters. Methylene chloride and several polar solvents have higher EF and OCEF than benzene, but none of the single solvents covers all the polarity range of the aerosol organics. Successive extractions using polar solvents, including water, after benzene extraction, indicate that an important fraction of aerosol organics, up to 48% as organic carbon, is missing using benzene extraction alone. All binary mixtures of a polar and a nonpolar solvent have higher OCEF than both polar and nonpolar solvents. Successive and binary mixtures extractions give identical OCEF results. Polar-solvent soluble inorganics, mostly nitrates, can be easily measured by difference using water extraction after polar solvent extraction. The validity of the OE–OCA technique is tested against several others. Among them, the direct OCA analysis of glass fiber filters is suggested. From 95 to 100% of the aerosol organic carbon is extracted and measured by the means of the proposed method, which seems particularly suitable for routine determination of atmospheric aerosol organic carbon.

Organic compounds are a significant fraction of the urban aerosols. Their concentration is usually measured by organic solvent extraction of samples collected on glass fiber filters (*1*). More detailed information is obtained by chemical analysis of the organic extracts: infrared (*2, 3*) and CHN analysis (*4, 5*), fractionation into classes (*5, 6*) and analysis of each fraction for specific compounds by TLC (*7*), GC (*8, 9*), UV–fluorescence (*10, 11*) and mass spectrometry (*12*). However, all these subsequent analyses depend on the organic solvent extraction efficiency (EF). Hydroxylic and other polar solvents show a good EF for organic particulate matter, but are able to dissolve a significant quantity of inorganics, especially nitrates, as well. Thus, in the absence of a suitable technique for routine organic carbon determination in those polar solvents, nonpolar solvents were most widely used in the past for the extraction of atmospheric organics. For example, benzene has been used for the National Air Surveillance Network (*13*) and numerous other studies (*4, 5, 8*). Among other solvents used are cyclohexane (*12, 14, 15*) because its EF is close to that of benzene and it is less toxic; CCl_4 (*16*) for its IR transparency and CS_2 (*17*) because of its very low flame ionization detector response in GC.

The purpose of this study is twofold: to show that extracting with benzene (or cyclohexane, or other nonpolar solvents) alone may lead to a serious underestimation of aerosol organics, and to describe a simple, accurate method