For the MCI₂, the mean ionic activity coefficients of each valence type were averaged from tabulated values (6). The average single ion activities in Table IV were estimated using the pH convention (7). Although this convention is properly applicable only at ionic strengths less than 0.1M, these activity coefficients are adequate for the present application.

LITERATURE CITED


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AIDS FOR ANALYTICAL CHEMISTS

Program ELAL: An Interactive Minicomputer Based Elemental Analysis of Low and Medium Resolution Mass Spectra

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In recent years, the popularity of the combination gas chromatograph–mass spectrometer (GC-MS) has increased markedly. This is due, in part, to the more stringent regulations set forth by OSHA and EPA requiring definitive identification of environmental contaminants. Another factor that contributed to this increase was the advent of the minicomputer based dedicated data system. This allowed for an efficient means of collection, reduction, and analysis of large volumes of data, thus making feasible, for many laboratories, an instrument that was once considered only a tool of research.

This rapid increase, however, has created a deficiency in the number of qualified mass spectrometrists needed to operate the large number of new instruments and interpret the data they provide. Therefore, many laboratories rely heavily upon the use of libraries of reference spectra and computerized search routines for definitive identification of unknowns (1). Although these are useful tools that aid in identification, invalid conclusions can often result when these methods are used alone. The practice of confirming the identification of unknown spectra by analyzing a reference standard is an excellent but not always practical procedure. The diligent use of elemental analysis can help the typical support laboratory reach more reliable conclusions, while significantly reducing turnaround time.

Although elemental analysis will not provide complete structural information, it does provide information as to the amounts of each element present. High resolution mass spectrometry is the most powerful method of determining elemental composition; however, the effects of the abundances of naturally occurring isotopes in low and medium resolution spectra can also lead to the elemental composition of many ions.

Many mass spectrometrists, because of inexperience and the time involved, fail to compute an elemental analysis on each unknown analyzed in the laboratory. With a dedicated minicomputer at their disposal, this chore can be readily handled. It was for this reason, program ELAL was developed. The program will compute an elemental analysis on low or medium resolution spectra for C, N, H, Cl, Br, F, S, Si, O, and P.

EXPERIMENTAL

ELAL was designed to be a callable subroutine that can be included as a part of existing GC-MS software or as a separate program that can be used when the data system is not in use. The program asks for only five items of information: the mass and intensities of the (A) peak and the intensities of the (A + 1), (A + 2), and the (A + 4) peaks. Either normalized or raw data may be entered. Computation is based on a modification of the manual method of elemental analysis described by McLafferty (2). With this method, elements are categorized as (A), (A + 1), or (A + 2) elements depending upon the prevalence of isotopes having 1 or 2 additional mass units. Thus, Cl with isotopes of 35 and 37 amu is considered an (A + 2) element. The common (A) elements are H, F, and P; the (A + 1) elements are C and N; and the (A + 2) elements are Cl, Br, Si, O, and S.

RESULTS AND DISCUSSION

After the requested data are entered, ELAL normalizes them and then uses the abundance of the (A + 1) peak to compute the number of carbons present. By means of a binomial expansion, the contribution of carbon to the (A + 2) peak is determined. The (A + 2) elements are then computed in order of decreasing isotopic abundance. If sulfur and/or silicone are found to be present, ELAL corrects for their contribution to the abundance of the (A + 1) peak and then completely recalculates the (A + 1) and (A + 2) elements. The contribution of oxygen to the (A + 1) peak is usually insignificant, so a correction need not be performed. Checkpoints are provided throughout the program to ensure that ELAL has not calculated an erroneous number of atoms for any one element. Chlorine and bromine are computed simultaneously by subtracting the abundances of
The authors thank R. M. Tuggle for his assistance during the development of this program.

CONCLUSIONS

ELAL will perform an accurate analysis as long as the mass spectrometer is in a reasonable state of tune. The constants used in the program were derived assuming a maximum mass abundance error of 5% of the theoretical abundance. Almost all instruments, if well adjusted and maintained, will operate within these limits. These constants can and should be changed if the program is to be used with an instrument that continuously maintains a higher degree of accuracy. Alternate constants have been derived for 2% error and can be supplied with the program. ELAL is written both in Hewlett-Packard Basic and Fortran. (The Fortran or Basic listing of the program and a users guide is available from the address listed above.) The Fortran used is compatible with many of the minicomputers used with GC-MS data systems. Hewlett-Packard Basic is a truly conversational language and can easily be translated into the Basic languages supported by other minicomputer manufacturers. The core requirement for the Basic interpreter and ELAL is 8K words. The compiled Fortran version requires 4K words.

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Random Error Propagation by Monte Carlo Simulation

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In general, a result or set of results $y_i$ are calculated from a number of experimental quantities $x_j$ but the $x_j$ are uncertain due perhaps to determine and/or random (indeterminate) errors. To project these errors into the resultant $y_i$ is a topic treated in many analytical and physical chemistry texts under the title of "error propagation". I wish to focus here on the particular problem of calculating the "most probable" uncertainty or error $\delta y_i$ in $y_i$ due to random errors $\delta x_j$ in the $x_j$. The "most probable" uncertainty is to be distinguished from the "maximum probable" error, this latter quantity estimating the maximum excursion expected of the results $y_i$ from the (unknown) true values which can be rationalized by the $\delta x_j$. This maximum by nature overestimates the most probable error.

A formula for the most probable propagated random error is commonly given (1, 2) as

$$
(\delta y_i)^2 = \sum_j \left( \frac{\partial y_i}{\partial x_j} \right)^2 (\delta x_j)^2
$$

(1)

The validity of this expression is based on a number of assumptions: (a) the various $\delta x_j$ are statistically uncorrelated; (b) the $x_j$ are functionally independent; and (c), if the $y_i$ are not linear functions of the $x_j$ then each $\delta x_j$ must be sufficiently small relative to the corresponding mean values of the $x_j$ so that the functions can be reasonably linearized about the means. If one or more of these assumptions is invalid, Equation 1 can be suitably corrected but at the expense of computational effort. A more difficult problem arises when the functional forms $y(x_j)$ are differentiable only with great difficulty or perhaps not at all. This problem, however, could be attacked by numerical methods.

The technique of Monte Carlo simulation is an alternative approach to be considered when Equation 1 or its corrected form is inconvenient and when digital computing facilities are available to handle the substantial and repetitive calculations. It has been applied to various problems in engineering, economics, and industrial operations (3), but is relatively unfamiliar to chemists.

Calculational Method. The random error propagation calculation under consideration in this paper is generally attempted only when the $\delta y_i$ are required but when these cannot be determined directly by repeating the experiment enough times for statistical validity. Clearly, if the experiment could be done repeatedly to generate a reasonable statistical population of each $y_i$ value, then the information on the random uncertainty in the $y_i$ would be in hand. The digital computer offers a convenient means of simulating the repetition. It is only necessary to generate new sets of $x_j$ data values, calculate the resultant $y_i$ values and store these for later statistical analysis. The repeated sets of $x_j$ could be generated in accordance with any distribution function, but the Gaussian (normal) serves to represent fluctuation in most physical situation.

Experienced scientific programmers should have little difficulty with this straight-forward calculation, but for those readers wishing to adapt a written program to their own problem, one is hereby offered with the following features and limitations: 1) Written in FORTRAN IV language. 2) Accepts $j \leq 20$ $x_j$ values and their uncertainties $\delta x_j$ assumed to be uncorrelated standard deviations. 3) Calculates $i \leq 20$ $y_i$ results and their standard errors (estimated standard deviations) $\delta y_i$. 4) Simulates $n \leq 100$ repetitive experiments based on the assumption that the $x_j$ values scatter normally. 5) Prints out calculated mean values and estimated standard deviations of the $y_i$.

A program listing and operating instructions will be sent without charge upon request to the author. The operator, in addition to writing his own subroutine relating his $y_i$ to $x_j$, must select the number $n$ of simulated repetitions. This choice is to be based on a trade-off between computer running time and the degree of certainty required of the calculated $\delta y_i$ values. A quantity which may be helpful in making this choice is the standard error (estimated standard deviation) in $\delta y_i$ which is given by $(\delta y_i)^2 = 2n(n-1)$ and which is derived for normal distributions (4) but is an approximation for others. Reference (4) also describes how confidence limits may be estimated for $\delta y_i$.

Sample Calculation. The following problem illustrates application of the technique. The primary dissociation constant $pK_1$ of a dibasic acid is to be calculated from a potentiometric pH titration of 50.00 ± 0.05 ml of 0.0563 ± 0.0005F solution of the disodium salt Na2A with HCl solution beyond the first equivalence point. The second dissociation constant $K_2$ is known to be 0.00538 ± 0.00012. After addition of 7.00 ± 0.01 ml of 0.634 ± 0.003 F HCl, the pH is 1.525 ± 0.002. Each of these six expressed uncertainties $\delta x_j$ are measured or estimated standard deviations. The desired result $pK_1$ is calculated from the following set of coupled equations which represent the equilibria, stoichiometry, and activity coefficient correlation.

$$
pK_1 = -\log K_1 = \frac{1}{2} \left( [H^+] [HA^-] \right)

[H^+] = 10^{pH - 7}

\log \gamma_A = -0.51V + 2.0V

[HA^-] = \frac{2CV(V + v) - [H^+] - C_{K1}CV}{1 + \frac{2K_1}{[H^+]}}

[A^{2-}] = \frac{K_2[HA^-]}{[H^+]\gamma_A}

[H_2A] = \frac{CV}{V + v} - [HA^-] - [A^{2-}]

I = \frac{1}{2} \left( [H^+] + [HA^-] + 4[A^{2-}] + \frac{C_{K1}CV + 2CV}{V + v} \right)

LITERATURE CITED


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