

APPLICATION OF PERSONAL MICROCOMPUTERS IN THE ANALYTICAL LABORATORY—I POTENTIOMETRIC ANALYSIS

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Summary—A novel general-purpose interface-controller unit has been designed and applied in potentiometric analysis. The unit is operated by a personal microcomputer programmed in BASIC. The interface-controller permits direct reading of specific ion-electrodes and can activate, under program control, laboratory instruments such as motor-driven burettes. The interface-controller is expandable to 16 analogue input channels, 16 binary (logic) input lines and 16 control relays but requires only one microcomputer I/O port (a total of 9 I/O lines) to handle all operations. Analogue to digital conversion is realized by counting, with the microcomputer, the output frequency of an analogue-to-frequency converter. This inexpensive method is effective in rejecting interfering signals such as power-line interference. The system has been applied in potentiometric titration analysis for determining the apparent dissociation constants of carbonic acid in sea-water and Dead Sea brines, and for ammonia determination with a gas-sensing electrode.

It is evident that the availability of cheap microprocessors and associated devices will eventually revolutionize the analytical laboratory¹ by automation of many operational, control and computation tasks which at present are performed manually. This end could be reached by interfacing existing analytical equipment with general purpose microcomputers or by designing new microprocessor-based analytical instruments. The latter approach is pursued by a number of commercial companies.

In this paper we present the alternative approach, namely the use of a general purpose microcomputer and general purpose interface operated by a high-level language. This approach has two advantages. It allows computerization of existing instrumentation and reprogramming at any stage to meet a specific need of the user, in contrast to microprocessor instrumentation which is controlled by fixed firmware. Various systems of that type were recently described by Anderson *et al.*²

Martin and Freiser³ have described a microcomputer-controlled potentiometric analysis system based on a commercial microcomputer, digital pH-millivolt meter and digital burette, operated by a high-level language (CONVERS) developed at the University of Arizona. Our study differs from that of Martin and Freiser in several respects. We use a more universal high-level language (BASIC) and have developed a

novel general-purpose interface which includes a high-resolution but cheap analogue to digital conversion scheme and high-impedance buffers for direct connection of pH and ion-selective electrodes. This interface can be operated in conjunction with any microcomputer which includes one 8-bit I/O port and a control line.

In this paper we describe the interface-controller and demonstrate its application in potentiometric analysis. The range of applications of this approach seems virtually unlimited.

INTERFACE DESIGN

The interface (Fig. 1) comprises 16 analogue inputs, 16 digital I/O lines and 16 uncommitted control relays. Analogue to digital (A/D) conversion is accomplished by first applying voltage to frequency (V/F) conversion and then measuring the frequency with the microcomputer. This simple and inexpensive A/D method was chosen on the basis of the intended applications, which do not call for a high rate of sampling. The method has the distinct advantage of rejecting interfering a.c. signals.

Analogue signals are fed to the V/F converter through a 16-channel multiplexer which operates under computer control. The impedance seen at the input of the analogue multiplexer is essentially the input impedance of the V/F converter, which is about 15 M Ω . Some of the channels are buffered by a very

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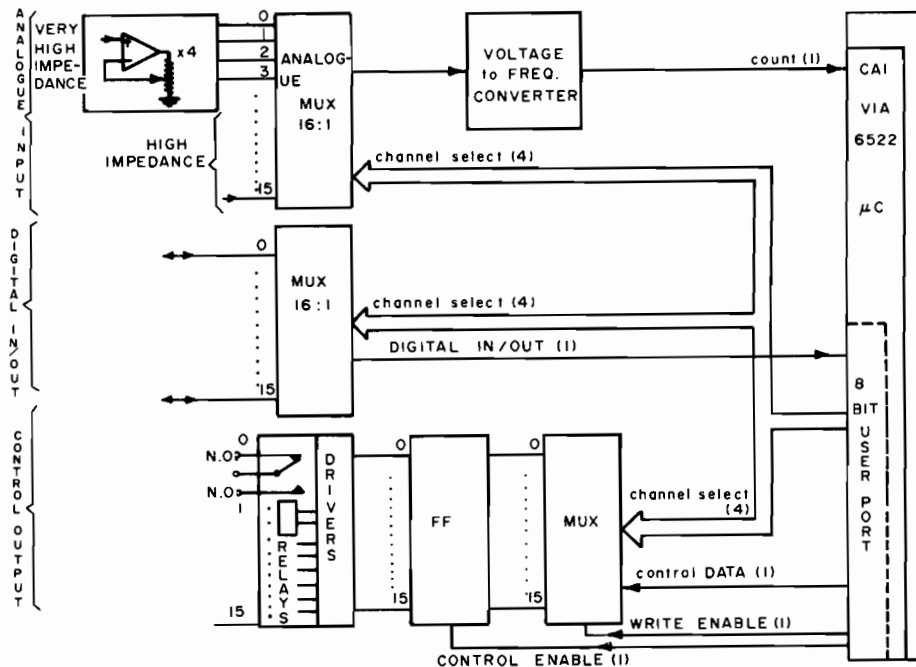


Fig. 1. Block diagram of proposed interface-controller.

high input impedance amplifier (MOSFET INPUT) to permit direct connection of pH and ion-selective electrodes. A second 16-channel multiplexer is used as a digital I/O port. Any of the lines can be a binary input or an output line. The interface-controller also includes 16 relays which are operated one at a time by the microcomputer.

Figure 1 shows a typical interconnection between the interface-controller and a microcomputer, which includes a versatile interface adaptor (VIA, type 6522). This type of interface is but one possibility, as the interface-controller is compatible with any system which has an 8-bit I/O port plus an additional binary input line for inputting the frequency signal, though it is required that any of the 8-bit lines can be programmed independently as an input or output line.

The interface-controller was built from a CMOS integrated circuit to minimize port loading and power consumption. The system used by us (Fig. 2) is, of course, just one approach of the many possible.

Figure 2a is the circuit diagram of half of the interface-controller. The complete 16 channel system is obtained by connecting two such sub-units in parallel. One half should have a break at point A of the printed circuit, and the other at point B, for proper channel decoding.

The control lines of the interface-controller are grouped as follows: PA0-PA3 (inclusive) are channel code lines. A binary combination on these lines will select one of the 16 channels of the analogue multiplexer, the digital multiplexer and one of the relay drivers. However, a relay flip-flop will be set or reset by PA4 only if line PA6 is enabled. An additional

control line PA5 is used to deactivate the relays as required on turn-on or default. Digital input/output is channelled through PA7 and the output frequency of the V/F is fed to the microcomputer through line CA1.

The V/F converter (Fig. 2b) is built around a monolithic unit (RC4151 Raytheon, Inc.) and the input is buffered by a CMOS operational amplifier (CA3140, RCA). Full range is adjusted by P_1 and the offset by P_2 (Fig. 2b). In the applications considered here, the output frequency range of 0-10 kHz corresponded to an input voltage range from -500 to +500 mV. Hence, the basic sensitivity (slope) under these conditions was 10 Hz/mV.

Analogue to digital conversion

Digitization is accomplished in the system by counting the pulses of the V/F converter over a fixed period of time by a subroutine written in assembly language for maximum speed. Execution time per incoming pulse is about 100 μ sec, corresponding to an upper frequency limit of 10 kHz. With a 1-sec counting window, the resolution is thus 1 part in 10^4 (ca. 13 bits) which is 0.1 mV. Digitization noise, estimated at $\pm 1/2$ pulse, is thus 86 db.

Besides the inherent sampling noise, the effect of integration on the signal-to-noise (S/N) ratio has to be considered. The counting technique used smooths the noise by integrating it over the counting period. Assuming a sinusoidal interfering noise of amplitude S_n , frequency ω_n and a randomly distributed phase angle ϕ_n , the total input signal S_i to the V/F is:

$$S_i = S_{in} + S_n \sin(\omega_n t + \phi_n) \quad (1)$$

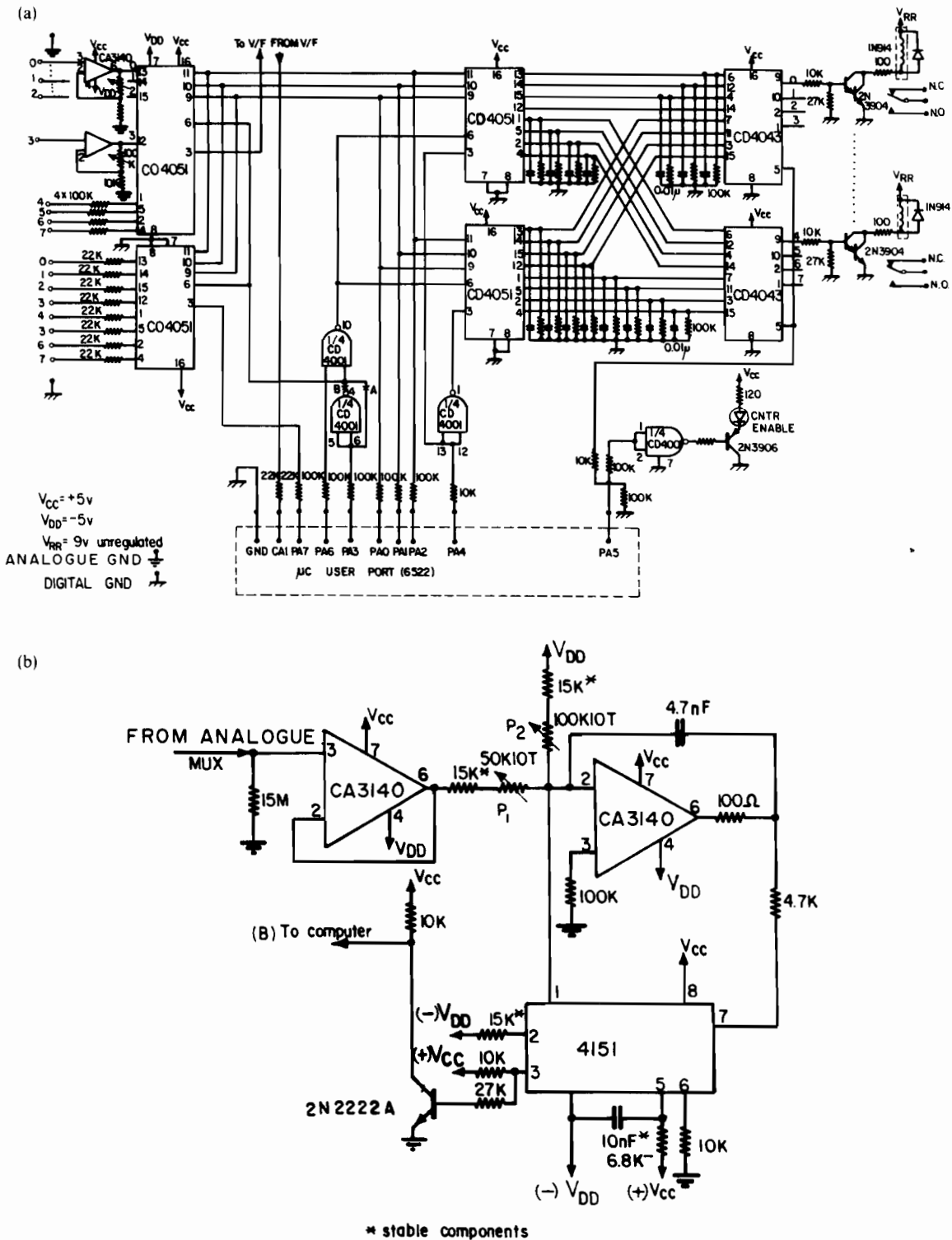


Fig. 2. Circuit diagram of interface-controller (a) and detailed circuit of V/F converter (b); 16-channel operation is obtained by using two units of type (a), one with a cut in the printed circuit at point A and the other with a cut at point B (shown in the 1/4 CD 4001 above PA3 in the user port).

where S_n is the useful input signal, which is assumed to be constant over the integration window T . Assuming linearity in the V/F conversion and neglecting sampling errors, the average total integrated (counted)

signal will be

$$\bar{S}_i = \frac{1}{T} \int_0^T [S_{in} + S_n \sin(\omega_n T + \phi_n)] dt \quad (2)$$

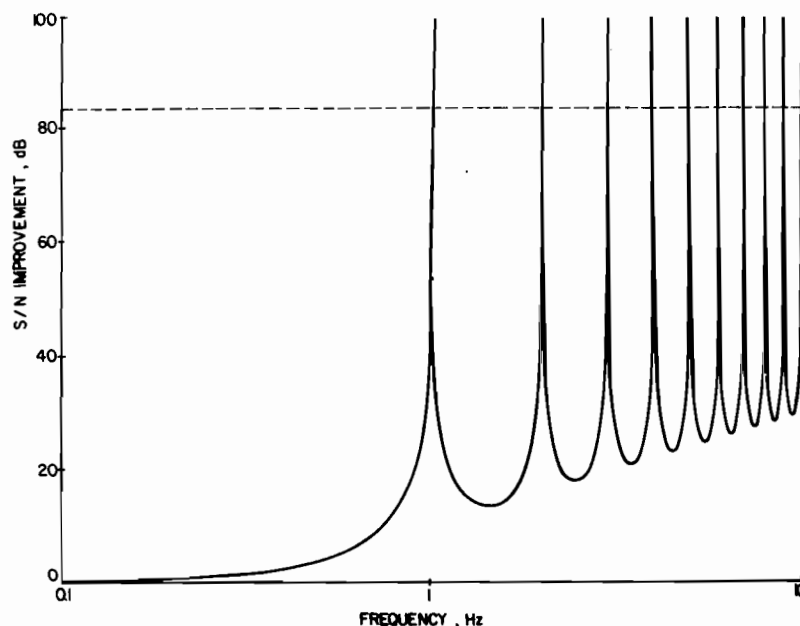


Fig. 3. S/N improvement obtained by the proposed A/D converter when the A/F frequency is counted for 1 sec. The broken line is the inherent digitization S/N (86 db) for a $1:10^4$ resolution, as used here.

$$\bar{S}_i = S_{in} + \frac{S_n}{\omega_n T} [\cos(\phi_n) - \cos(\omega_n T + \phi_n)] \quad (3)$$

The S/N ratio at the input is:

$$(S/N)_{in} = \frac{S_{in} \sqrt{2}}{S_n} \quad (4)$$

and the expected S/N ratio after integration becomes:

$$(S/N)_0 = \frac{S_{in} \omega_n T}{\sqrt{2} S_n |\sin(\omega_n T/2)|} \quad (5)$$

The improvement in S/N is thus:

$$\frac{(S/N)_0}{(S/N)_{in}} = \frac{\omega_n T}{2 |\sin(\omega_n T/2)|} = \frac{\pi(T/T_n)}{|\sin(\omega_n T/2)|} \quad (6)$$

where T_n is the period of the interfering signal.

The expected improvement in S/N was calculated and plotted over the frequency range 0.1–10 Hz (Fig. 3). The broken line sets the limit of the maximum sampling error which, for a 0–10 kHz conversion range, is 86 db. The actual improvement was measured by feeding to the V/F converter a d.c. signal on which a sinusoidal signal was superimposed. It was found that the expected and actual improvement agreed very well (Fig. 4).

The effect of counting-period variation on the S/N improvement was measured by changing the counting window while corrupting the input signal with a constant interfering noise derived from the mains (50 Hz). The agreement between calculated and measured S/N improvement (Fig. 5) is good, considering the slight instability of the mains frequency and uncertainty in the counting window. The mismatch corresponds to

about 0.1% variation in frequency or counting period, which is well within the tolerance of the set-up.

The ability to adjust the counting window to give optimum S/N improvement, *i.e.*, maximum rejection of an interfering noise with a given frequency, could be very useful in noisy environments. Since the mains frequency is a major interfering noise, the counting window should be adjusted for maximum rejection of this frequency. Optimum performance could be obtained by adjusting the counting window under software control to give maximum S/N improvement.

EXPERIMENTAL

Titration assembly

The titration system (Fig. 6) comprised a CBM type 2016 microcomputer (Commodore Business Machines, Inc.), the interface-controller described above, a Metrohm motor-driven burette, type E415 and a titration vessel in a thermostatic bath. The burette delivered 0.1-ml increments of titrant under program control by one relay of the interface-controller.

The sensor electrode was connected to a buffered channel of the interface controller and the reference electrode to the electrical ground of the electronics.

Electrodes

A Metrohm combination pH electrode, type EA 120, and a Broadly James NH_3 gas-sensing electrode, type 7010, were used.

Acid-base titrations

Mediterranean sea-water and Dead Sea brines were titrated with 0.5M hydrochloric acid. The titration was fully automatic and under microcomputer control. The titration procedure included four cycles (Fig. 7): (a) manual input of titration parameters; (b) the titration cycle; (c) storage of raw data; (d) data processing.

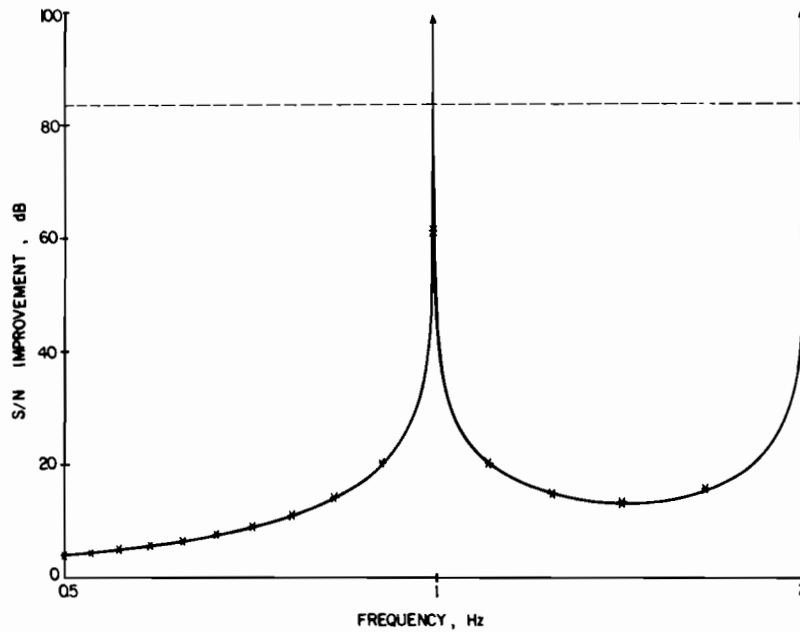


Fig. 4. Calculated (solid line) and measured (asterisks) S/N improvement in the proposed A/D converter for the frequency range 0.5–2 Hz.

Ammonia determination

The ammonia and the glass combination electrodes were connected to the interface controller through three high input impedance buffers and ground. The reference of the pH-electrode was grounded and all other lines, including the internal reference electrode of the ammonia electrode, were buffered to eliminate ground-loop problems. The pH of the solution (which had fixed ammonium chloride concentration) was adjusted manually by addition of 10M sodium hydroxide after addition of 2 ml of NBS standard pH-4 buffer,⁴ and the outputs of the two electrodes were read by the microcomputer. These data were later used to obtain the best estimate of the constant required for calcu-

lating the total ammonia concentration from the readings of the ammonia and pH electrodes.

Computer programs

All programs, except the short subroutine for measuring the frequency of the V/F converter, were written in BASIC.

RESULTS AND DISCUSSION

Carbonate determination

The method was extensively used for studying the carbonate system in Dead Sea brines and mixtures of

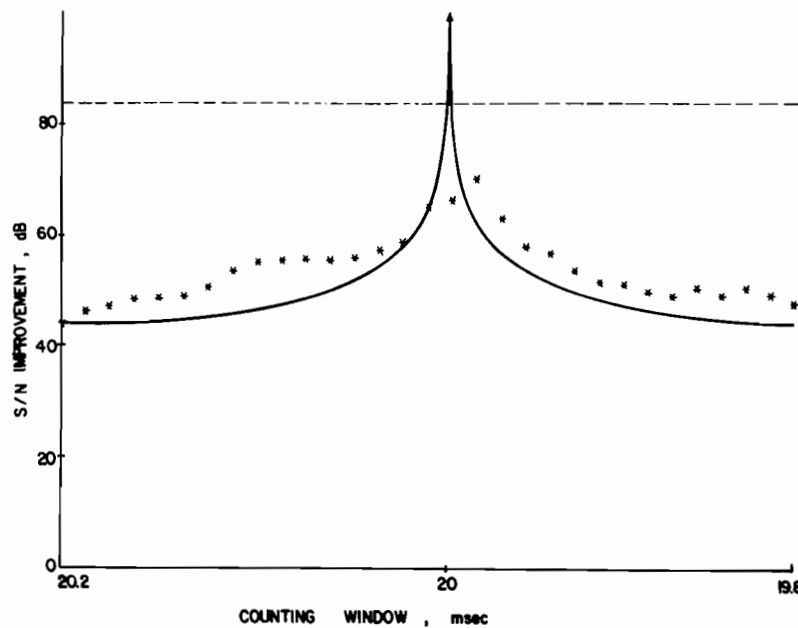


Fig. 5. S/N improvement in the proposed A/D converter as a function of counting-window width for a 50-Hz interfering signal.

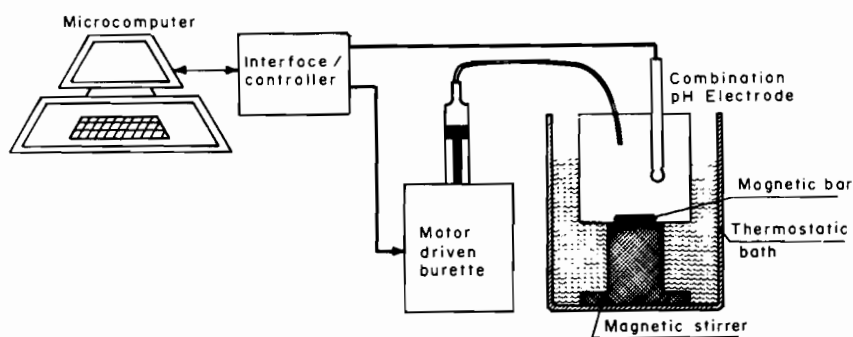


Fig. 6. Experimental system for automatic titration.

Dead Sea brines and Mediterranean sea-waters, to determine the alkalinity and first and second apparent dissociation constants of carbonic acid (K'_1 and K'_2) in the test solution. The procedure followed that described earlier by Sass and Ben-Yaakov.⁵

K'_1 and K'_2 of carbonic acid are used extensively by oceanographers⁶ to describe the carbonate system in sea-water and other natural waters. The constants are defined in terms of measurable parameters:

$$K'_1 = \frac{a_{H^+} \cdot [HCO_3^-]}{[H_2CO_3]} \quad (7)$$

$$K'_2 = \frac{a_{H^+} \cdot [CO_3^{2-}]}{[H_2CO_3]} \quad (8)$$

where the brackets stand for total concentrations of the free and complexed species and a_{H^+} is the activity of the hydronium ion as determined by a glass electrode. Hence, the apparent constants are practical parameters, the use of which eliminates the need to estimate single-ion activity coefficients in complex solutions such as sea-water. However, since the constants are dependent on the ionic strength and composition of the solution, they must be determined for each case separately. They can be calculated from the pH readings during a hydrochloric acid titration. The calculation procedure⁵ is basically a least-squares fit of the titration data to the model equation which describes the dependence of pH on the amount of acid added, by use of equations (1) and (2), an alkalinity mass-balance, and assumption that the total concentration of CO_2 species is constant. The alkalinity is first determined by a Gran-type titration.^{5,8} The computation procedure is done by a BASIC program run after the titration is completed.

Typical titration curves obtained with the system are shown in Fig. 8. The results obtained for the sea-water ($pK'_1 = 5.95$, $pK'_2 = 9.00$) agree well with Lyman's values (5.98 and 9.06).⁶

Ammonia determination

The ammonia gas-sensing electrode responds only to NH_3 and is insensitive to the ammonium ion.⁹

Since the distribution of total ammonia (ΣNH_3) between NH_3 and NH_4^+ is pH-dependent, ΣNH_3 can be directly determined by the electrode only at pH high enough for practically all the ammonia to be in the molecular form. If the ammonia and water dissociation constants

$$K_{NH_3} = \frac{[NH_4^+][OH^-]}{[NH_3]} \quad (9)$$

$$K_w = [OH^-][H^+] \quad (10)$$

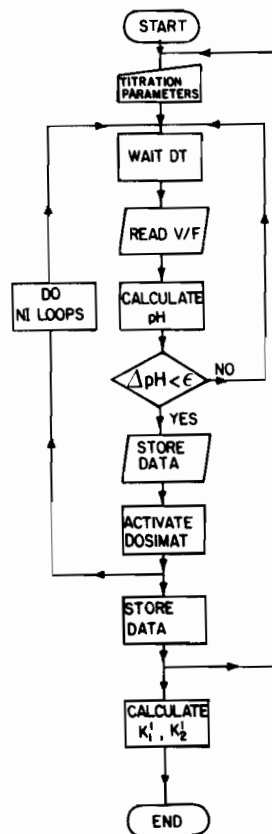


Fig. 7. Flow diagram of the titration procedure.

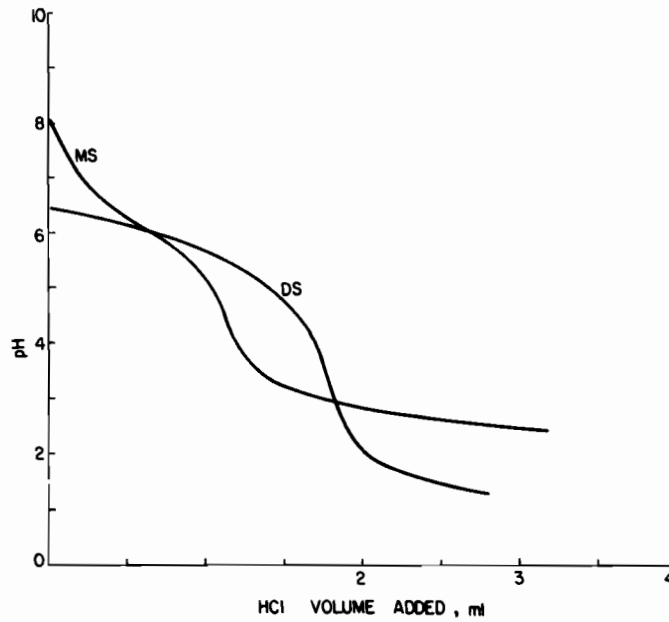


Fig. 8. Typical titration curves for Mediterranean sea-water (MS) and Dead Sea brine, obtained by the proposed system. Solutions were titrated with 0.5M HCl.

are known, ΣNH_3 can be calculated¹⁰ from the readings of the ammonia and pH electrodes and the relationships

$$\Sigma \text{NH}_3 = [\text{NH}_3] \left\{ 1 + \frac{K_{\text{NH}_3}[\text{H}^+]}{K_w} \right\} \quad (11)$$

$$[\text{NH}_3] = 10^{(E_{\text{NH}_3}^0 + S_{\text{NH}_3} \cdot V_{\text{NH}_3})} \quad (12)$$

$$[\text{H}^+] = 10^{(E_{\text{H}^+}^0 + S_{\text{H}^+} \cdot V_{\text{H}^+})} \quad (13)$$

where E^0 , S and V are the potential offset, slope and

mV reading of the electrode designated by the subscript.

Direct determination of ΣNH_3 from pH and $[\text{NH}_3]$ by equation (4) is not always possible since K_{NH_3}/K_w is a function of the ionic composition of the solution and is seldom known. We have used the microcomputer system described here to calculate this constant for a given test solution by a trial and error calculation method. The procedure compares calculated ΣNH_3 values with the actual concentration for a series of guessed values for K_{NH_3}/K_w . This procedure

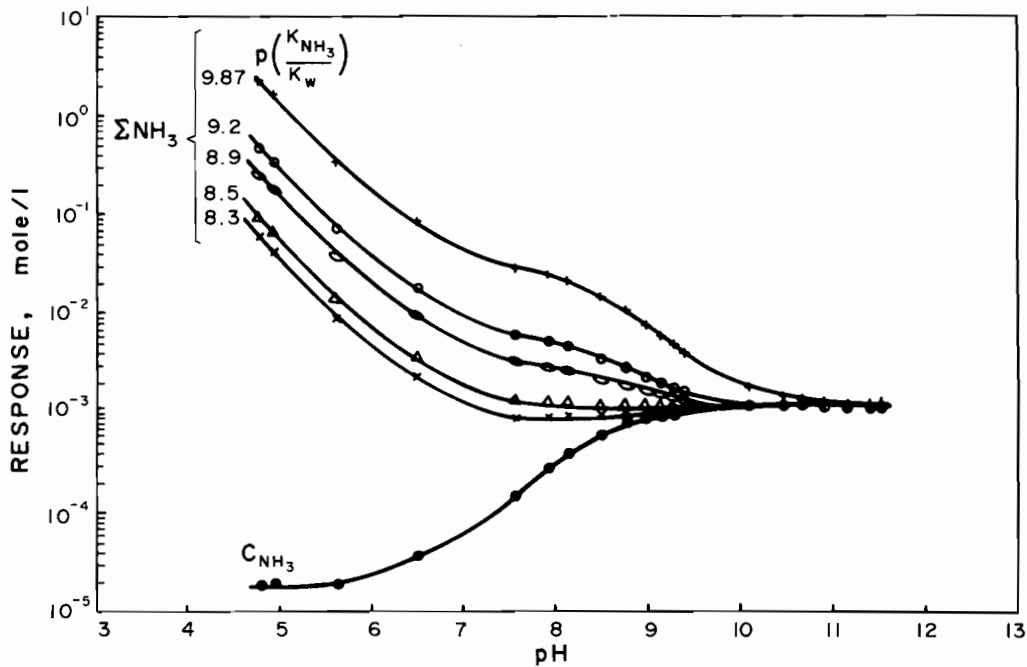


Fig. 9. Response of ammonia electrode in $10^{-3}M \text{NH}_4\text{Cl}$ at various pH values (lower curve), and calculated ΣNH_3 , for various guessed values of K_{NH_3}/K_w .

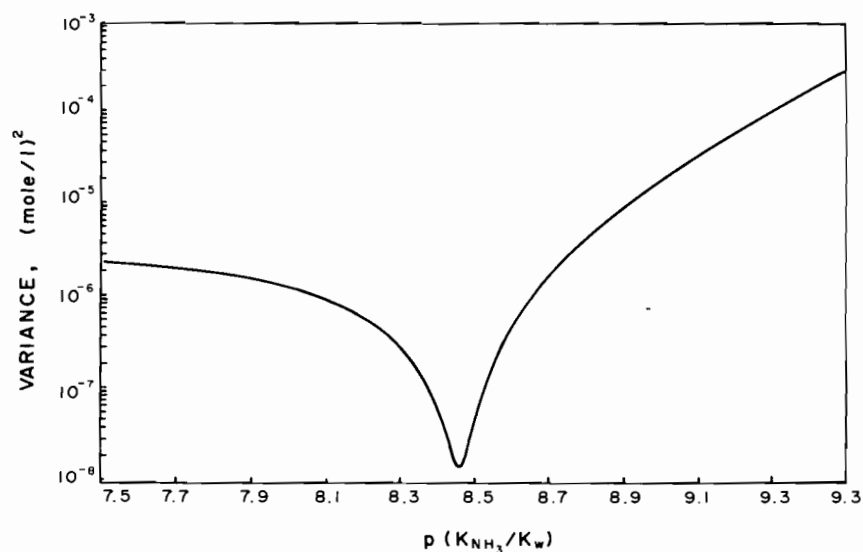


Fig. 10. Variance of the difference between calculated ΣNH_3 and known value (as measured at high pH) for various values of guessed K_{NH_3}/K_w . (For data of Fig. 9.)

is summarized graphically in Fig. 9 which depicts the original NH_3 -electrode data and calculated ΣNH_3 for a number of K_{NH_3}/K_w values. The variance of the difference between the calculated values and the known concentration (as measured at high pH) was then used to find the best fit (Fig. 10). Once the constant is determined for a given solution it can be used to calculate ΣNH_3 from the reading of the electrodes at any pH provided the free ammonia concentration is not below the lower limit of linear response of the ammonia electrode. As this limit for the ammonia electrode used was about $2 \times 10^{-5}M$, ΣNH_3 at the $0.002M$ level could be determined at any pH not below 7.5 (Fig. 9).

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