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VALTER, A COMPUTING PROGRAM FOR AUTOMATIC THERMOMETRIC TITRATIONS

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ABSTRACT

A simple automatic system for thermometric titrations is described. This system is based on the use of a Wheatstone bridge, an automatic burette, a digital potentiometer, both with RS232C interface, and a portable IBM PC computer.

This system is very versatile and software for different research and routine applications is given.

INTRODUCTION

Interest in automation has greatly increased with the introduction of laboratory microcomputers.

From 1978 onwards several papers on the general use of microprocessors [1–5], and others referring to potentiometry [6–10], spectrophotometry [11], electroanalytical techniques [12–15], kinetics [16], etc. have been published.

Most of the systems described are based on the use of cheap microprocessors programmed in assembly [3,16–22]. Interfaces for interconnection with scientific instruments have been dealt with in other publications [23–25].

Due to the lack of an automatic thermometric titration apparatus, we decided to assemble an appropriate system in order to facilitate both experimental and computing work.

Owing to the great difficulties present in assembly programming and the skill necessary to build up and program interfaces, we considered it to be more convenient to exploit the advantages offered by the popular personal microcomputers; these are easily programmed in BASIC, and some already have the RS232C interface compatible with scientific instruments.

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EXPERIMENTAL

Apparatus

The following apparatus was used: (1) a thermometric system, described elsewhere [26,27], provided with a 100 kΩ thermometer-type thermistor; (2) a direct current amplifier with ×10 gain; (3) a Crison Digilab 517 potentiometer, with RS232C interface and ±0.1 mV precision; (4) a Crison 738 autoburette, with RS232C interface; (5) a Houston Omniscribe register; (6) a portable IBM PC microcomputer, provided with 256 kb of RAM memory and RS232C interface; and (7) a Fujitsu 2200 printer.

The protocol of the RS232C interfaces for both potentiometer and burette has been previously described [28].

Reagents and solutions

All solutions were prepared from analytical grade reagents and dissolved in distilled water.

System description

The block diagram of the microcomputer-controlled system is shown in Fig. 1.

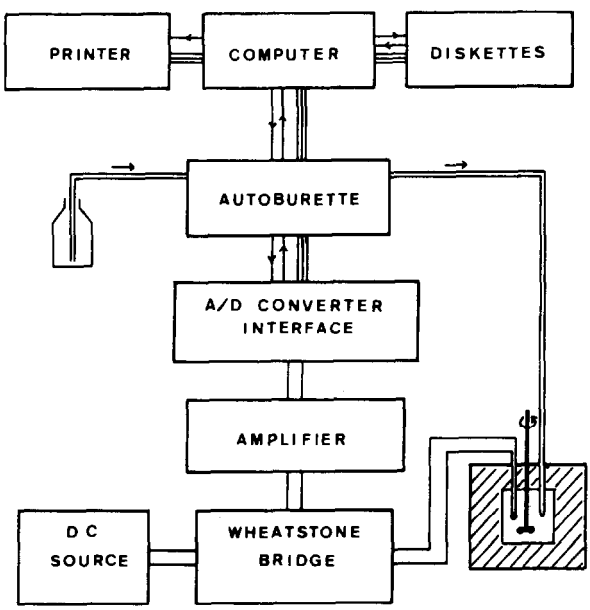

Fig. 1. Block diagram of the microcomputer controlled system.

This system consists of a portable IBM PC connected by the serial port to the burette and potentiometer, which is used as an A/D converter. The Wheatstone bridge for temperature measurements, based on the use of a thermometer-type thermistor, is connected to the electrodes' input of the potentiometer through a $\times 10$ amplifier. This direct amplifier is used to adapt the voltage output of the bridge to take advantage of the full scale range of the potentiometer. A heat calibration system is included in the same bridge module, and is employed both to determine the heat capacity of the cell and rapidly reach the initial temperatures selected for the thermometric titrations. The thermometric cell consists of a screw type polystyrene beaker kept in a Dewarflask, which is, in turn, surrounded by a block of porexpan.

PROGRAM

The program VALTER * was developed from consideration of the following requirements:

(1) The user's convenience. The user can select different options by means of a menu, which facilitates the use of the program by non-skilled personnel.

(2) Data storage on disc and optional printer output.

(3) Optional data manipulation; data can be graphically represented as a thermometric curve, or as its first or second derivative. End points can be either manually or automatically calculated by means of linear extrapolation.

Flow diagram

The flow diagram of VALTER is presented in Fig. 2. After the program presentation, the main menu is displayed on the screen allowing four options: (1) an experimental titration to be performed; (2) data to be introduced manually; (3) an experiment to be retrieved from a data file, and (4) the program work to be finalized.

When options (1), (2) or (3) are selected, the computer asks if the printer will be used during the program, in order to offer the possibility of printing out some results in different parts of the program.

If the experimental titration or the manual data input are selected, then the general conditions of the experiment (titrant reagent and concentration,

* The VALTER program for IBM PC or compatible computers can be applied for from the Bank of Programs, Department of Chemistry, University of Balearic Islands, E-07071 Palma de Mallorca, Spain.

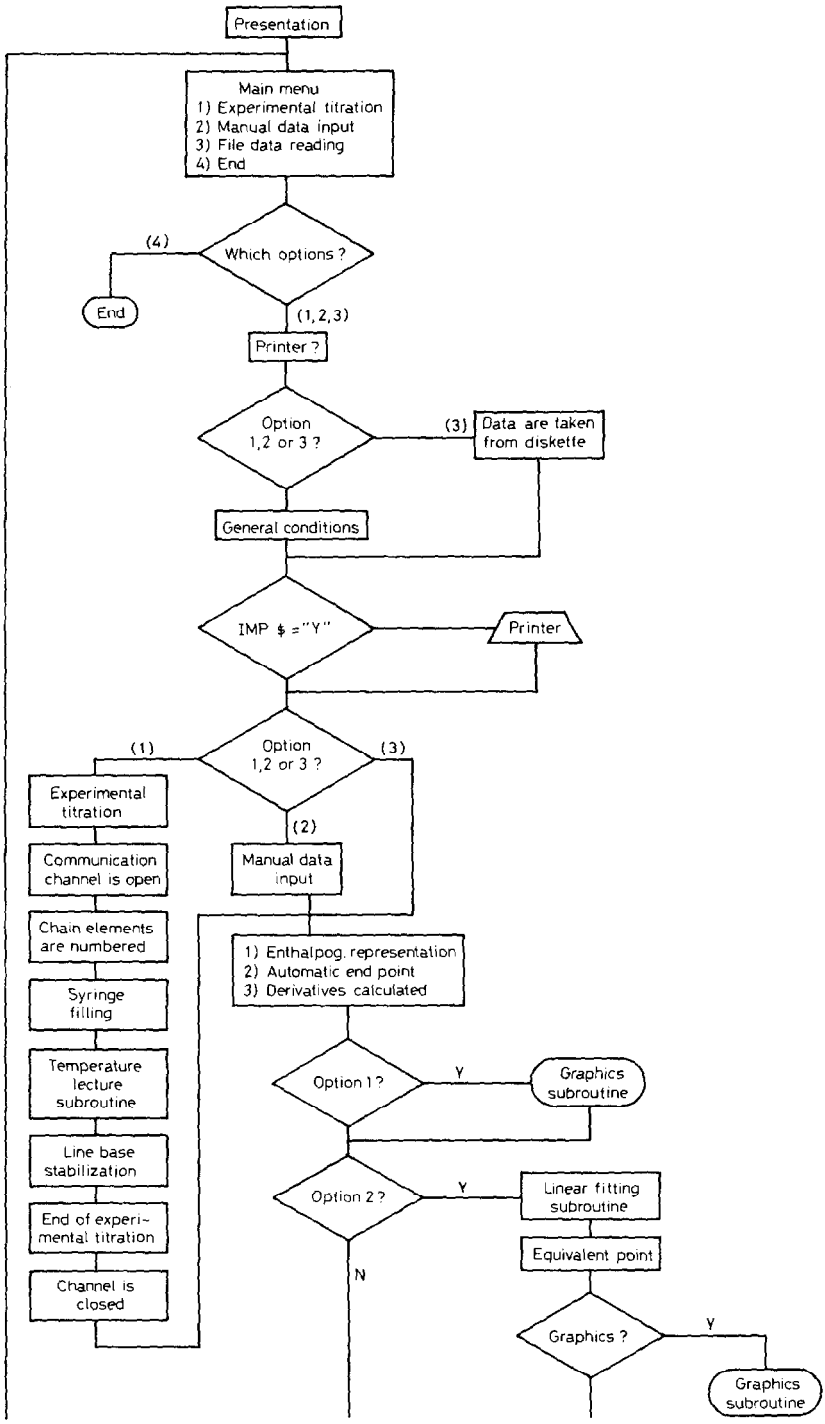

Fig. 2. Flow diagram of the program VALTER.

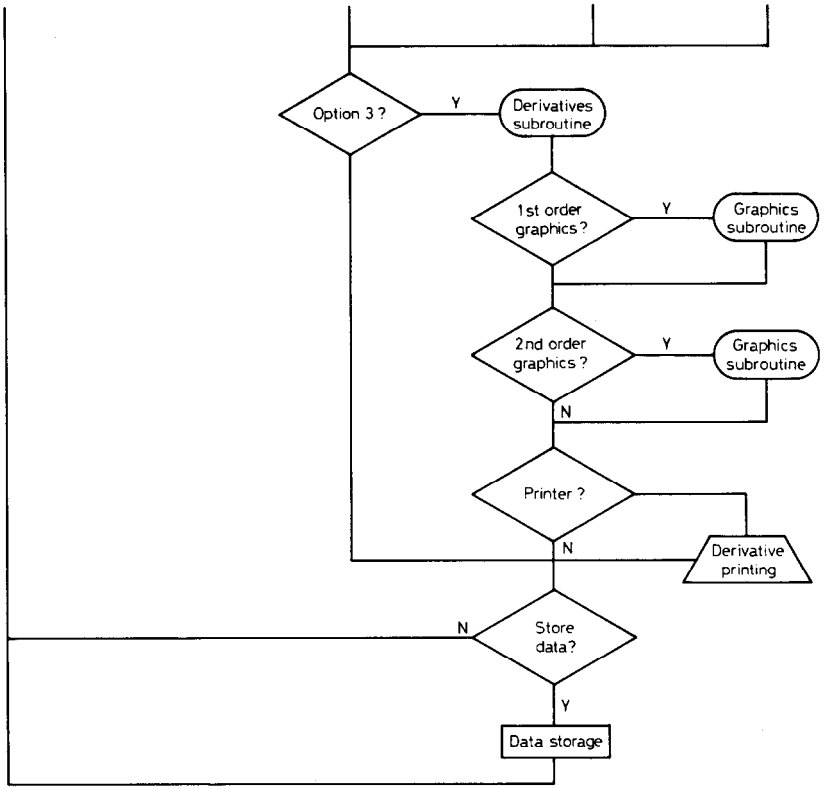

Fig. 2. Continued.

remarks, ionic strength, sample volume, etc.) are requested and stored in the data file output. Optionally, they can also be printed as hard copy.

After these general questions, the experimental titration begins by opening the communication channel and assigning an order number to the burette and potentiometer. The burette syringe is filled and the temperature baseline is made inferior to a preselected value introduced in the general conditions; then a prefixed number of temperature measurements are stored and the thermometric titrations begin. The temperature curve is stored in the RAM memory until the selected desired volume has been injected.

Once the experimental data have been automatically or manually introduced, several options are then presented in a successive order: enthalpograms can be displayed on the screen and a hard copy can be obtained. The appropriate linear regressions can be calculated in order to automatically obtain the initial and end points and, hence, the equivalence point. First and second derivatives can be reached and graphically represented. In all cases, all results optionally can be printed as hard copy. Finally, the experimental points may be stored in a selected name data file output.

RESULTS

Our experience with the program VALTER has been very positive, since it greatly facilitates the experimental task, which can be performed automatically with the experimental data being stored on magnetic support.

These data files can be conveniently reused or modified by an ASCII word processor, as WORDPROOF of SPFPC, for direct use by the MINITERM program, which was developed for thermodynamic parameter refinements (log β_i, ΔH) [29].

In Table 1 a hard copy of an experimental titration is presented. In Fig. 3 a thermometric curve for (a) a strong and (b) a weak base can be seen. Due to the high pK_b value of pyridine, its standardization had to be carried out in glacial acetic acid. When the thermometric titration is performed, its curve is as well shaped as for a strong base (unlike Gibbs titrations).

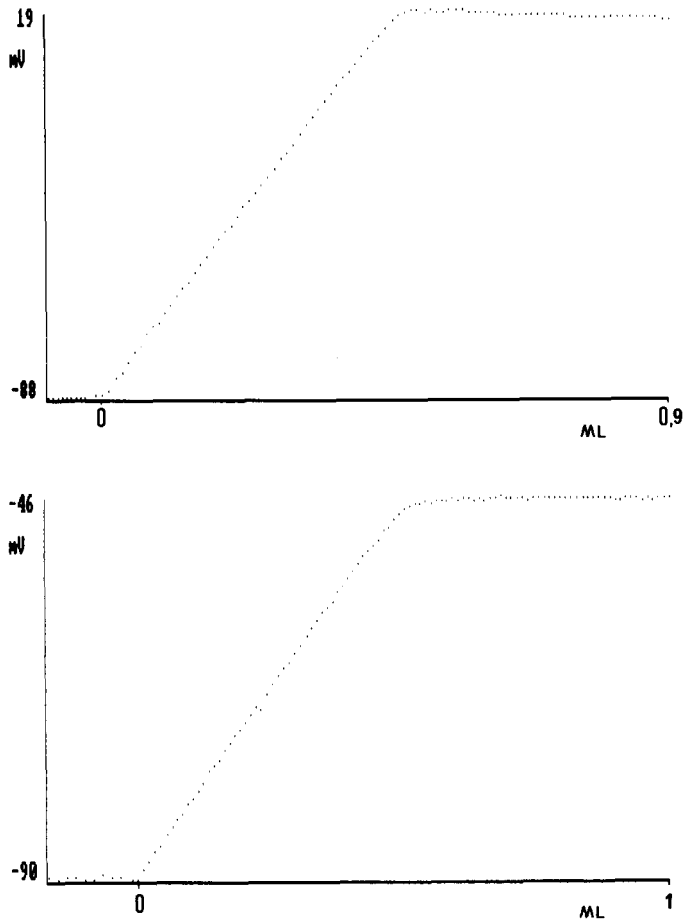

Fig. 3. (a) Thermometric titration of NaOH with HCl; (b) thermometric titration of pyridine with HCl.

TABLE 1

Hard copy of an experimental titration [a]

N	Time (s)	Volume (ml)	Temp. (mV)	N	Time (s)	Volume (ml)	Temp. (mV)
1	2.85	−0.16	−89.3	56	90.24	0.45	−50.7
2	5.27	−0.14	−89.5	57	91.56	0.46	−49.7
3	7.63	−0.12	−89.2	58	92.93	0.47	−49.2
4	9.99	−0.11	−89.1	59	94.30	0.48	−48.3
5	12.41	−0.09	−89.4	60	95.62	0.49	−47.8
6	14.77	−0.07	−89.4	61	96.99	0.50	−47.2
7	17.13	−0.06	−89.0	62	98.37	0.51	−46.9
8	19.49	−0.04	−89.2	63	99.74	0.52	−46.7
9	21.91	−0.02	−89.3	64	101.06	0.53	−46.6
10	25.04	0.00	−89.4	65	102.43	0.54	−46.3
11	26.36	0.01	−89.4	66	104.13	0.55	−46.8
12	27.73	0.02	−88.3	67	105.51	0.56	−46.4
13	29.11	0.03	−87.6	68	106.83	0.57	−46.5
14	30.81	0.04	−86.4	69	108.20	0.58	−46.3
15	32.18	0.05	−85.8	70	109.57	0.59	−46.2
16	34.21	0.06	−84.4	71	111.27	0.60	−46.5
17	35.53	0.07	−83.5	72	112.59	0.61	−46.1
18	36.90	0.08	−82.6	73	113.97	0.62	−46.1
19	38.28	0.09	−81.9	74	115.34	0.63	−46.3
20	39.60	0.10	−80.9	75	116.71	0.64	−46.2
21	40.97	0.11	−80.1	76	118.03	0.65	−46.4
22	42.34	0.12	−79.2	77	119.73	0.66	−46.2
23	43.72	0.13	−78.5	78	121.11	0.67	−46.2
24	45.42	0.14	−77.1	79	122.48	0.68	−45.8
25	46.74	0.15	−76.3	80	123.80	0.69	−46.2
26	48.11	0.16	−75.7	81	125.17	0.70	−46.0
27	49.48	0.17	−74.5	82	126.87	0.71	−46.1
28	50.86	0.18	−73.7	83	128.25	0.72	−46.2
29	52.17	0.19	−73.0	84	129.62	0.73	−46.3
30	53.55	0.20	−72.4	85	130.94	0.74	−46.1
31	54.92	0.21	−71.5	86	132.31	0.75	−46.1
32	56.24	0.22	−70.6	87	134.01	0.76	−46.1
33	57.61	0.22	−69.8	88	135.33	0.77	−46.2
34	58.98	0.23	−70.0	89	136.70	0.78	−46.0
35	60.69	0.25	−68.1	90	138.08	0.79	−46.0
36	62.01	0.26	−67.1	91	139.45	0.80	−46.2
37	63.71	0.27	−66.1	92	140.77	0.80	−46.0
38	65.08	0.28	−65.2	93	142.47	0.82	−46.1
39	66.45	0.29	−64.6	94	144.17	0.83	−46.1
40	67.83	0.30	−63.5	95	145.55	0.84	−46.2
41	69.53	0.31	−62.8	96	146.92	0.85	−46.2
42	71.23	0.32	−61.6	97	148.24	0.86	−46.1
43	72.55	0.33	−60.8	98	149.94	0.87	−46.0
44	73.92	0.34	−59.8	99	151.31	0.88	−46.2
45	75.30	0.35	−58.9	100	152.69	0.89	−46.3
46	76.62	0.36	−58.3	101	154.01	0.90	−46.5
47	77.99	0.37	−57.6	102	155.38	0.91	−46.1

(continued)

TABLE 1 (continued)

N	Time (s)	Volume (ml)	Temp. (mV)	N	Time (s)	Volume (ml)	Temp. (mV)
48	79.36	0.38	−56.7	103	156.75	0.92	−46.2
49	80.68	0.39	−56.0	104	158.13	0.93	−46.2
50	82.05	0.40	−55.2	105	159.83	0.94	−46.4
51	83.43	0.40	−54.3	106	161.15	0.95	−46.2
52	84.80	0.41	−53.5	107	162.52	0.96	−46.3
53	86.12	0.42	−52.6	108	163.89	0.97	−46.1
54	87.49	0.43	−51.8	109	165.60	0.98	−46.2
55	88.86	0.44	−51.4	110	166.91	0.99	−46.1

[a] Experiment number, 1; remarks, 10 ml pyridine 0.0489 M; titrant, HCl; titrant concentration, 0.9196 M; sample to titrated, pyridine; initial volume, 50 ml; ionic strength, 0.1 M; input file name, PIR3; output file name, OUTNAME; final injected volume, 1 ml; syringe volume, 1 ml.

In Table 2, the results for a strong and a weak base can be compared when they are titrated with a strong acid. As was expected, the results are better for a strong base, both for accuracy and precision. However, the weak base cannot be titrated directly in aqueous solution by other methods.

Manual calculation of the equivalence points gives the best results. There are some difficulties in selecting the appropriate criteria for linear extrapolations, owing to the curvature of the thermometric titration, difference in temperature between titrant and titrand, etc.

The worst results were obtained when the first derivative curve was used to calculate the equivalence point. Although there are no computing prob-

TABLE 2

Titration errors of NaOH and pyridine [a] with HCl

Compound	Amount (meq)	Manual		Automatic		First derivative	
		Amount found (meq)	ε (%)	Amount found (meq)	ε (%)	Amount found (meq)	ε (%)
NaOH	0.2165	0.2082 ± 0.004	−3.8	0.2041 ± 0.012	−5.7	0.208 ± 0.026	−3.6
	0.3031	0.3019 ± 0.007	−0.4	0.3096 ± 0.002	2.1	0.321 ± 0.020	+5.8
	0.4330	0.4305 ± 0.004	−0.6	0.4254 ± 0.015	−1.8	0.424 ± 0.020	−2.0
	0.6495	0.6516 ± 0.027	0.3	0.6547 ± 0.011	0.8	0.648 ± 0.021	−11
Pyridine	0.2445	0.2306 ± 0.005	−5.7	0.2245 ± 0.004	−8.2	0.224 ± 0.002	−8.3
	0.3423	0.3372 ± 0.005	−1.5	0.3258 ± 0.013	−4.7	0.324 ± 0.011	−5.1
	0.4890	0.4753 ± 0.009	−2.8	0.4779 ± 0.017	−2.3	0.482 ± 0.007	−1.3
	0.5868	0.5656 ± 0.014	−3.6	0.5542 ± 0.008	−5.5	0.567 ± 0.002	−3.4
	0.7335	0.6873 ± 0.005	−6.3	0.6838 ± 0.009	−6.8	0.654 ± 0.034	−11

[a] Purity of pyridine was 95.59%, determined by non-aqueous titration with $HClO_4$ in glacial acetic acid.

TABLE 3

Refinement of pK and ethalpy values of pyridine with MINITERM

Vol. (ml)	pH	Tot. L	Tot. M	T, m	T, c	D
0.021	6.634	0.100E+01	0.000E+00	0.00050	0.00183	−0.00133
0.030	6.472	0.100E+01	0.000E+00	0.00170	0.00262	−0.00092
0.040	6.339	0.100E+01	0.000E+00	0.00240	0.00350	−0.00110
0.052	6.214	0.100E+01	0.000E+00	0.00340	0.00456	−0.00116
0.061	6.137	0.100E+01	0.000E+00	0.00470	0.00535	−0.00065
0.071	6.062	0.100E+01	0.000E+00	0.00540	0.00623	−0.00083
0.080	6.001	0.100E+01	0.000E+00	0.00600	0.00703	−0.00103
0.092	5.929	0.100E+01	0.000E+00	0.00740	0.00810	−0.00070
0.101	5.880	0.100E+01	0.000E+00	0.00870	0.00890	−0.00020
0.111	5.829	0.100E+01	0.000E+00	0.00950	0.00979	−0.00029
0.123	5.772	0.100E+01	0.000E+00	0.01050	0.01086	−0.00036
0.132	5.732	0.100E+01	0.000E+00	0.01160	0.01166	−0.00006
0.142	5.690	0.100E+01	0.000E+00	0.01240	0.01256	−0.00016
0.151	5.653	0.100E+01	0.000E+00	0.01300	0.01337	−0.00037
0.161	5.614	0.100E+01	0.000E+00	0.01420	0.01427	−0.00007
0.173	5.569	0.100E+01	0.000E+00	0.01560	0.01535	0.00025
0.182	5.536	0.100E+01	0.000E+00	0.01610	0.01617	−0.00007
0.192	5.501	0.100E+01	0.000E+00	0.01700	0.01707	−0.00007
0.201	5.470	0.100E+01	0.000E+00	0.01830	0.01789	0.00041
0.215	5.422	0.100E+01	0.000E+00	0.01960	0.01916	0.00044
0.227	5.382	0.100E+01	0.000E+00	0.02010	0.02026	−0.00016
0.239	5.343	0.100E+01	0.000E+00	0.02130	0.02136	−0.00006
0.258	5.282	0.100E+01	0.000E+00	0.02330	0.02310	0.00020
0.268	5.250	0.100E+01	0.000E+00	0.02440	0.02402	0.00038
0.277	5.221	0.100E+01	0.000E+00	0.02500	0.02482	0.00018
0.286	5.192	0.100E+01	0.000E+00	0.02630	0.02565	0.00065
0.296	5.160	0.100E+01	0.000E+00	0.02690	0.02657	0.00033
0.306	5.128	0.100E+01	0.000E+00	0.02750	0.02750	0.00000
0.318	5.088	0.100E+01	0.000E+00	0.02880	0.02861	0.00019
0.327	5.059	0.100E+01	0.000E+00	0.02970	0.02945	0.00025
0.336	5.028	0.100E+01	0.000E+00	0.03060	0.03029	0.00031
0.346	4.994	0.100E+01	0.000E+00	0.03150	0.03122	0.00028
0.358	4.952	0.100E+01	0.000E+00	0.03270	0.03234	0.00036
0.368	4.916	0.100E+01	0.000E+00	0.03330	0.03327	0.00003
0.377	4.883	0.100E+01	0.000E+00	0.03430	0.03411	0.00019
0.386	4.848	0.100E+01	0.000E+00	0.03540	0.03496	0.00044
0.396	4.809	0.100E+01	0.000E+00	0.03610	0.03590	0.00020
0.405	4.772	0.100E+01	0.000E+00	0.03690	0.03674	0.00016
0.415	4.729	0.100E+01	0.000E+00	0.03820	0.03768	0.00052
0.424	4.688	0.100E+01	0.000E+00	0.03860	0.03853	0.00007
0.434	4.640	0.100E+01	0.000E+00	0.03970	0.03947	0.00023
0.448	4.568	0.100E+01	0.000E+00	0.04080	0.04079	0.00001
0.457	4.517	0.100E+01	0.000E+00	0.04190	0.04163	0.00027
0.467	4.456	0.100E+01	0.000E+00	0.04270	0.04257	0.00013
0.477	4.388	0.100E+01	0.000E+00	0.04350	0.04350	0.00000
0.486	4.320	0.100E+01	0.000E+00	0.04460	0.04433	0.00027
0.498	4.217	0.100E+01	0.000E+00	0.04560	0.04542	0.00018

(continued)

TABLE 3 (continued)

Vol. (ml)	pH	Tot. L	Tot. M	T, m	T, c	D
0.508	4.115	0.100E+01	0.000E+00	0.04620	0.04630	−0.00010
0.517	4.007	0.100E+01	0.000E+00	0.04680	0.04706	−0.00026
0.527	3.867	0.100E+01	0.000E+00	0.04740	0.04783	−0.00043
0.538	3.689	0.100E+01	0.000E+00	0.04740	0.04852	−0.00112

Q, 0; P, 1; R, 1; log β, 5.206; ΔH (cal mol^{-1}), −5707. ΔH metal = 0.000E+00; ΔH lig. = 0.000E+00. Square of residuals = 0.1381E−04; Standard deviation = 0.5309E−03; Error of parameter No. 1 = 1.913671E−02; Error of parameter No. 2 = 22.43696.

lems, the random noise in the thermometric system leads to badly defined first derivative curves (Fig. 4). For the same reasons, the second derivative thermometric curves can hardly be used for practical purposes. An improved system is obviously needed when the first and second derivatives must be systematically used.

In Table 3 are displayed the results achieved when the experimental data obtained by VALTER were used in combination with the program MINITERM.

CONCLUSIONS

The modular systems based on the use of PC computers and RS232C interfaces present a great number of advantages over other completely integrated systems:

(1) Standard PC computers are becoming more and more compact, light, quick, and are more powerful and cheaper than dedicated microprocessors.

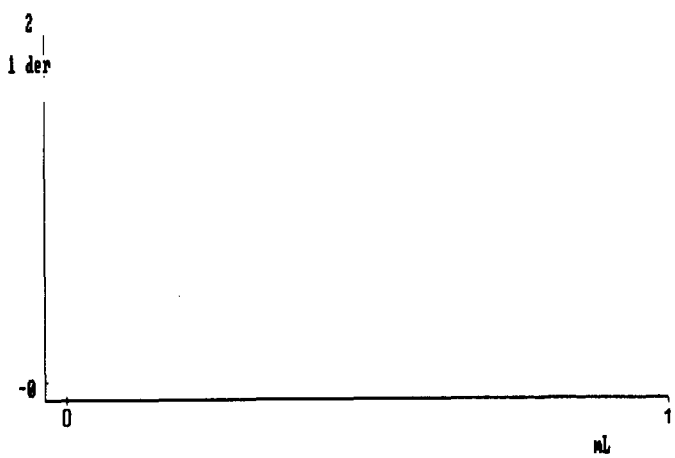

Fig. 4. First derivative corresponding to a titration of NaOH with HCl.

(2) BASIC programming and RS232C standard interfaces allow unskilled users to build up their own more convenient systems.

(3) The modular concept allows the use of different components, which can be quickly reordered for other practical purposes, like potentiometric [28], spectrophotometric and kinetic applications.

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REFERENCES

1 J.C. Smit and H.C. Smit, Anal. Chim. Acta, 143 (1982) 45.
2 J.C. Smit, H.C. Smit, H. Steigstra and U. Hannema, Anal. Chim. Acta, 143 (1982) 79.
3 A.H.B. Wu and H.V. Malmstadt, Anal. Chem., 50 (1978) 2090.
4 F.E. Woodward, W.S. Woodward and C.N. Reilley, Anal. Chem., 53 (1981) 1251A.
5 G. Horlik, Talanta, 28 (1981) 487.
6 G. Velinov, N. Todorov and S. Karamphilov, Talanta, 30 (1983) 687.
7 T. Pap, M. Molnar and J. Inczdy, J. Automatic Chem., 3 (1981) 198.
8 H. Gampp, M. Maeder, A. Zuberbhler and T.A. Kaden, Talanta, 27 (1980) 513.
9 T. Pap, M. Molnar and J. Inczdy, Mag. Kem. Foly., 86 (1980) 567.
10 D.J. Legget, Anal. Chem., 50 (1978) 118.
11 Y. Iida, M. Furukarwa and S. Shibata, Bunseki Kagaku, 31 (1982) T65.
12 T. Wasa and H. Yamamoto, Bunseki Kagaku, 31, (1982) T55.
13 T. Wasa, H. Yamamoto and K. Akimoto, Bunseki Kagaku, 31 (1982) T95.
14 T. Wasa, H. Yamamoto and K. Akimoto, Bunseki Kagaku, 31 (1982) T21.
15 J.F. Price, S.L. Cooke and R.P. Baldwin, Anal. Chem., 54 (1982) 1011.
16 I.R. Bonnell and J.D. Defree, Anal. Chim. Acta, 134 (1982) 189.
17 H.Y. Cheng, W. White and R.N. Adams, Anal. Chem., 52 (1980) 2445.
18 D.J. Leggett, Talanta, 29 (1982) 189.
19 I.R. Bonnell and R.J. Dalle-Molle, Anal. Chim. Acta, 134 (1982) 179.
20 L. Petros, L. Sváb, V. Hynek and V. Svoboda, Chem. Listy, 76 (1982) 241.
21 E.D. Salin, M.W. Blades and G. Horlick, Talanta, 28 (1981) 519.
22 E.B. Buchanan and M.L. Buchanan, Talanta, 27 (1980) 947.
23 A. Pardo, Commodore Mag., 4 (1984) 38; and 5 (1985) 5.
24 S. Ben-Yaakov, R. Raviv, H. Guterman and A. Dayan, Talanta, 29 (1982) 267.
25 E.T. Lynk and S. Ludke, General Electric, Technical Information Ser., Rep. No. 80CRD094, May 1980.
26 J. Lumbiarres, C. Mongay and V. Cerdá, Analusis, 8 (1980) 62.
27 J. Lumbiarres, C. Mongay and V. Cerdá, J. Therm. Anal., 22 (1981) 275.
28 J. Maimó, M. Far, J.M. Estela and V. Cerdá, Quím. Anal., 5 (1986) 245.
29 V. Cerdá, J.M. Estela and R. Jara, Thermochim. Acta, 87 (1985) 13.