Automated Gravimetric Management of Solutions
Part 1. High-performance Microcomputer-controlled Gravimetric Burette

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A versatile gravimetric burette and the necessary interface that allows it to be controlled by an IBM-PC microcomputer are described. The burette employs an electronic balance that holds three 30 ml flasks. The flasks are used for delivering different titrants or standard solutions and are connected to the sensor through the bottom of the balance. The addition of the solution is controlled by poly(tetrafluoroethylene) electromechanical valves housed inside the unit. The flasks can be refilled automatically from larger reservoirs placed outside the case. Solution level sensors are used to realize automatic refill when necessary. The mass delivered from the flasks is read by the computer through an RS232C interface. The burette can, when driven by the appropriate software, perform potentiometric, biamperometric and spectrophotometric titrations, standard additions procedures and the preparation of standard solutions.

Keywords: *Gravimetric burette; titration; standard additions; automated titration*

The gravimetric addition of a solution in titration procedures has been described in the literature.[1-5] The advantages of such an approach to titrant addition are always emphasized: for example, it is claimed that gravimetric additions do not require any calibration of the glassware, and are free from errors caused by solution viscosity and by contraction/dilatation of the volume caused by a change in the ambient temperature. Moreover, additional advantages are provided by the use of modern electronic balances: for example, rapid weighing, absence of moving parts that can be affected by mechanical stress, and the balance frequently has a standard RS232 interface providing prompt communication with microcomputers.

In addition to these advantages the potential of the gravimetric approach has not yet been fully exploited. In fact, the gravimetric manipulation of solutions in the laboratory could lead to more precise and reliable results. On the other hand, there is a need for a versatile, cost effective, gravimetric apparatus to deal with the variety of analytical procedures that demand solution management.

Some of the instruments described previously do not guard against air currents which can affect the mass measurement. Therefore, high sensitivity balances cannot be used.[1,3,4] The instruments described also employ a large reservoir (and sometimes a control valve) placed on the balance plate. As the load on the balance is high, the usable sensitivity is only 0.01 g in those less expensive balances which can handle, for example, only 100 g with a sensitivity of 1 mg.

Previously described instruments do not allow the simultaneous use of more than one solution in the same gravimetric addition unit. The use of more than one solution with only one balance would improve the cost to benefit ratio of constructing the unit and at the same time would extend its ability to perform, for example, a back-titration, and simple or multiple standard additions procedures.

This paper describes a versatile microcomputer-controlled gravimetric burette that extends the application of such units and allows for the use of more than one solution per balance which can operate with a higher sensitivity.

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Experimental

Gravimetric Burette

The gravimetric burette is depicted in Fig. 1. The unit was constructed using a metallic frame 50 cm high, 25 cm wide and 25 cm deep. Three sides of the metallic frame were closed with metallic sheets and the front was closed with an acrylic sheet that can be lifted if access to the flasks inside the unit is desired. The metallic frame has a platform on which an Acatec Model BCM 1003 electronic balance with capacitive sensor was placed. The balance can operate with a sensitivity of 1 mg (maximum load 100 g) or 10 mg (maximum load 1000 g). At the top of the case there is a small metallic door through which it is possible to reach the balance plate. A metallic rod was connected to the sensor through a hole in the base of the balance case. At the end of the rod, an acrylic plate sustains three 30 ml polyethylene flasks held on the plate by inner plastic screws. At the base of the flasks a hole of 0.1 mm diameter was drilled for admission of air during solution delivery. The outlet of the flasks contains a 2.0 cm long, 1.6 mm o.d., 1.2 mm i.d., glass tube, to which is attached a 1.5 mm i.d. Tygon tube. The length of the Tygon tube is twice the distance between the glass tube and the three-way valves (NResearch Model 161TO31) to which the tubes are connected to the common port. The normally closed outlets of the valves are connected to poly(tetrafluoroethylene) (PTFE) tubes (20 cm × 0.9 mm i.d.). These tubes are taken out from the metallic case through small holes drilled in the front acrylic sheet and are used for solution delivery. The normally open outlets of the valves are connected to two-way valves (NResearch Model 161TO11) placed outside the case. These valves are connected to 1 l solution reservoirs placed on the outside of the case. The manifold used to couple the solution reservoir to the flasks inside the burette case is shown in Fig. 2. When any of the two-way valves is turned on the stock solution is delivered to the respective burette flask. When any of the three-way valves is turned on the solution present in the respective flask is delivered outside the case, through the PTFE tube. The mass, delivered during the period in which the valve is kept on, is monitored by the computer.

Around the small glass tube fitted at the outlet of each inner flask there is an infrared opto-switch (PCST-2103). The switches are used to detect when a flask is empty, requiring immediate action by the computer to turn on the respective two-way valve to refill the flask. The refill operation is

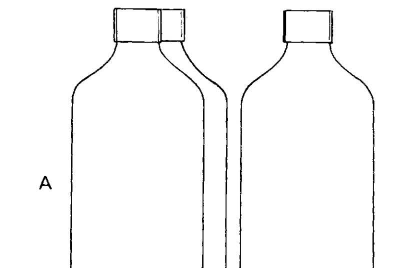

Fig. 1 Proposed gravimetric burette. A, External solution reservoir flasks; B, electronic balance; C, two-way electromechanical valves; D, internal flasks; E, three-way electromechanical valves; F, solution outlet; and G, metallic case

performed by switching the respective two-way valve on and by following the increase in the mass of the whole set of inner flasks. For the flasks used, a maximum mass increase of 20 g is allowed before the valve is switched off, stopping the operation. Therefore, no sensor for the 'full' status is required. The time spent on this operation can be reduced if a nitrogen pressure is applied to the external stock solution reservoir.

Interface and Electronic Circuits

The communication of the balance with the microcomputer (DICOM, IBM-PC XT compatible, 640 kbyte RAM, Winchester of 20 Mbyte and Floppy of 360 kbyte, Display CGA-monochrome) is made at 9600 bits s^{-1} using the serial RS232 interface present in both the balance and computer. The balance sends a string containing the mass reading every 0.3 s.

The control of the gravimetric unit is effected by using the asynchronous interface described previously.[6] The interface communicates with the microcomputer through a user port based on the CI 8255.[7] The card, containing the user port, is plugged into an extension slot inside the microcomputer. Two handshake signals (strobe and acknowledge), the ground line and the eight parallel data lines are exchanged between the computer user port and the interface.

A circuit diagram of the interface employed for control of the burette and for data acquisition is shown in Fig. 3. The CI 74LS373 (I) is used as an address decoder and up to eight electronic devices can be accessed.[6] Two of the addresses (254 and 253 corresponding to bit 0 and 1) are used for a dynamic

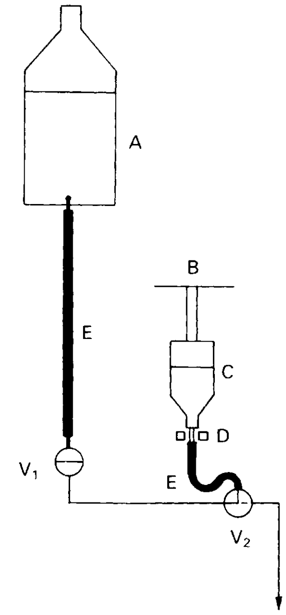

Fig. 2 Manifold to connect the external reservoir flasks to the internal burette flasks. A, External reservoir flask; B, balance support; C, burette flask; D, opto-switch; E, Tygon tube; F, burette outlet; V1, two-way valve; and V2, three-way valve

analogue-to-digital converter based on an 8 bit DA (ZN428) and an 8 bit AD (ZN448).[8] The address line 251 (bit 2) is connected to another 74LS373 (III) used as an 8 bit latch. Six of the output lines are used to source the base current to 2222N transistors, used as switches for the electromechanical valves.

Address line 243 (bit 3) is used to enable another CI 74LS373 (II), used to input the logic state of the three level sensors. A circuit diagram of the optical sensors is shown in Fig. 4. The average change in the voltage at the collector of the opto-transistor is 2.0 V (from 6.0 to 4.0 V). This change is caused mainly by the difference in the refractive index between the full and the empty glass tube. Therefore, approximately the same change is observed for coloured solutions such as 0.01 mol dm^{-3} $KMnO_4$ and 0.1 mol dm^{-3} $K_2Cr_2O_7$. The reference voltage for the 741 comparators is set to the middle of the range, about 5.0 V. When the level of liquid in the flask is above the limit the TTL logic level at the comparator output is high. The existence of a low level signs the 'flask empty' condition.

Analogue signals to be monitored are passed through an analogue input pre-conditioning stage. This stage (which is not shown in Fig. 3) is based on two OPO7 operational amplifiers and is designed to provide a high versatility in terms of the dynamic range and polarity of the signal to be followed. The first OP07 can supply a positive or negative gain to the signal. Its output is sent to the next stage which will sum a positive or negative offset voltage[9] to change a bipolar signal to a positive only signal which can be followed by the dynamic analogue-to-digital converter, shown in Fig. 3.

Main Software to Control the Gravimetric Burette

General use software to drive the user card and the interface, and for reading the dynamic analogue-to-digital converter, has been described previously.[7,8] In addition to this software, a number of QUICKBASIC 4.5 sub-programs were written specifically to control the gravimetric unit. These sub-programs are shown in the Appendix.

Five sub-programs are necessary to control the gravimetric burette. The SUB valveon(nv%) and SUB valveoff(nv%) are used to open or close, respectively, any of the six valves present in the gravimetric unit; nv% is the valve number (1–6). The sub-program SUB fillburette(n%,ma) is used to fill

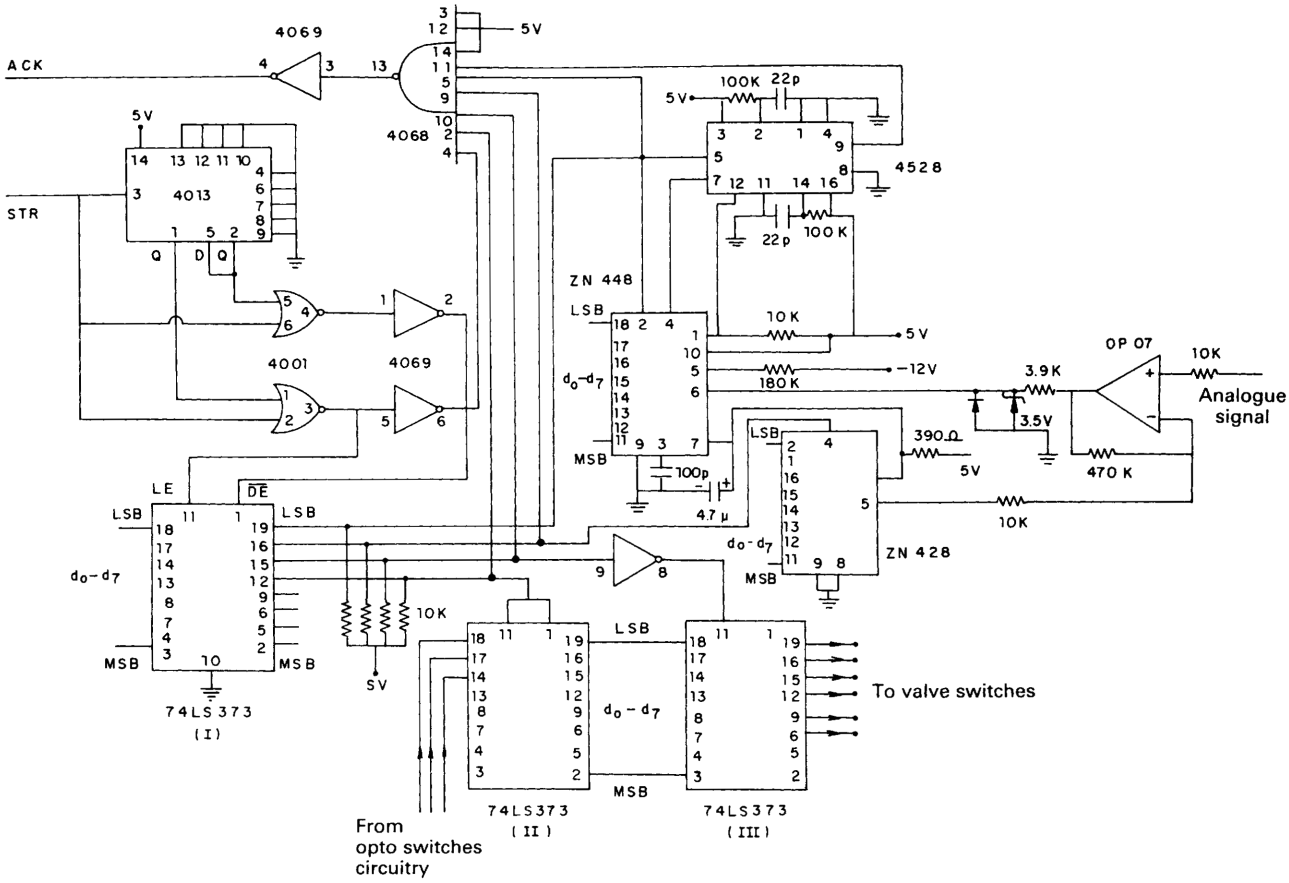

Fig. 3 Electronic circuit diagram of the interface employed for control of the burette and data acquisition

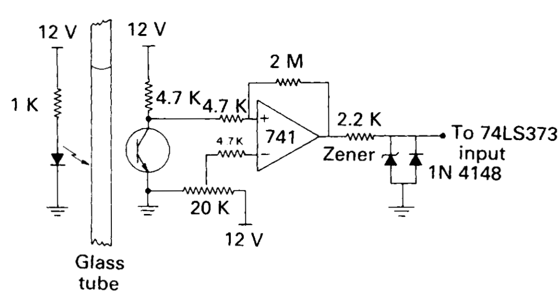

Fig. 4 Electronic circuit diagram for solution level detection

the burette flask n% (1–3). The flask n% will be empty to the optical sensor level and then refilled until a mass change equal to ma is observed. If the flask is already empty the refill operation is executed directly.

The sub-program SUB addtime(n%,t,madd) can be used to deliver the solution present in flask n% (1–3) for a fixed time interval t (in seconds). The sub-program checks if the flask is not empty and, in that situation, the SUB fillburette(n%,ma) is automatically called. The mass actually added is returned in the variable madd. The SUB addmass(n%,m, madd) is used to deliver a mass approximately equal to m from the flask n%; it also checks for the level of the solution. Again the added mass is returned in madd. The SUB readbalance(stb,flaginst-%,mass) is used to read the balance through the RS232 serial interface. Mass is the variable containing the mass reading, stb is the value for the reading stability test. If two consecutive readings agree in between this value the sub-program is exited and the flaginst% is set to 0. If more than ten readings are made the last value is returned in the 'mass' variable and the flaginst% is set to 1, indicating that the balance is unstable.

The above set of sub-programs are sufficient for the implementation of most of the titration or standard additions procedures.

Results and Discussion

The gravimetric burette was evaluated for its accuracy in transferring mass from the burette flask to the reaction flask outside the case. The burette flasks were filled with water and the sensitivity of the balance was set to 1 mg. The mass was transferred to a previously weighed glass flask. The mass transferred was determined with an analytical balance with a sensitivity of 0.1 mg. The values of mass accessed by the microcomputer from the burette balance(mt) were compared with those obtained with the analytical balance(mr). Results for 120 comparisons (ten trials for each delivery time interval: 0.5, 2.0, 5.0 and 10 s, for each burette flask) showed that the differences (mt − mr) were never higher than +0.002 g or lower than −0.002 g. The mt values are related to the mr values by the equation:

$$mt = (-8.17 \times 10^{-4} \pm 0.34) + (0.9989 \pm 1.2 \times 10^{-3})mr$$

the correlation coefficient is 0.99998 and the error of the estimate is 9.6×10^{-4} g. No systematic proportional or constant error between the two sets of measurements could be detected at the 95% confidence level.[10]

The flow rate of the gravimetric burette changes slightly as a function of the height of the liquid column inside the flasks. The change is not significant and does not alter the true measurement of the mass transferred. At the level of the bench the flow rate for a diluted aqueous solution is about 3.0 ml min^{-1}, if the manifold described under Experimental is employed. If it is necessary, an increase in the flow rate can be achieved by placing the case higher than the level of the bench or by using larger bore tubing to assemble the manifold.

The potentiometric titration curve for the titration of 5 ml of 0.01 mol dm^{-3} Fe^{II} solution with 0.001667 mol kg^{-1} $K_2Cr_2O_7$ solution, monitored by using a Pt electrode and an Ag–AgCl reference electrode, is shown in Fig. 5. The end-point was found using the second-derivative method. Note that the

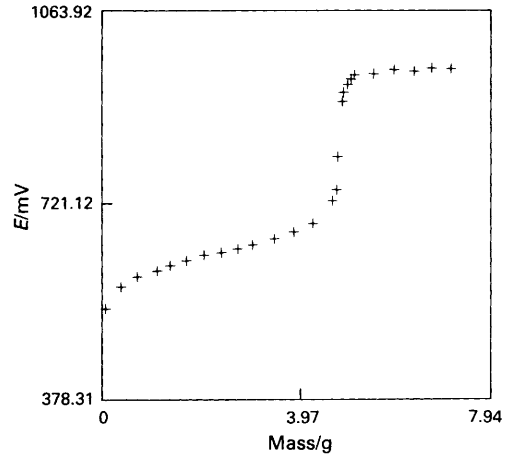

Fig. 5 Potentiometric titration curve obtained using the prototype gravimetric burette. Titrant, 1.667×10^{-3} mol kg^{-1} $K_2Cr_2O_7$; titrand, 0.01 mol dm^{-3} Fe^{II} solution

driven software is capable of slowing down the mass added near the end-point, permitting an increase in the precision of the determination. A sensitivity of 1 mg was employed in the burette balance in carrying out such titrations. The average of ten determinations and the standard deviation were $(1.007 \pm 0.007) \times 10^{-2}$ mol dm^{-3}. The precision is good considering the small (5 ml) sample volume titrated.

The gravimetric burette described here presents some advantages over previously described instruments. The unit is isolated from air currents, allowing the use of more sensitive balances. The same balance can be used with more than one flask, improving the cost to benefit ratio of constructing the unit. The total load of the accessories (support + empty flasks) is about 45 g. Therefore, it is possible to use high sensitivity balances in the construction of the burette. Refill of the burette is achievable and is performed automatically by the control program. The flasks do not need to be removed from the unit. Therefore, the over-all performance of the instrument is improved as factors affecting the weighing precision, such as a change in the condition of the tube connecting the flask to the valve, are not present.[3] The tube is always 'relaxed' as is necessary for good precision in mass transference.[3] The gravimetric unit can also be used to implement a totally gravimetric approach to a given analytical procedure. The mass of the sample (liquid or solid) can be found using the same balance of the unit, gaining access to the balance plate through the door at the top of the case. In so doing, it is important to keep the total load on the balance below the higher limit for the selected sensitivity.

Although three flasks were used in the prototype described here, it is possible to add more flasks to the unit. By using a sensitivity of 0.01 g, the total mass of the support plus flasks can be as high as 1000 g.

The atmosphere in the case can be kept inert (free of oxygen, for example) by maintaining a slight positive pressure of nitrogen. An inert atmosphere can be useful if one wishes to use the burette to perform standard additions in polarographic determinations, for example.

If compared with the modern volumetric addition units commercially available, the gravimetric unit can offer the same performance at low cost per individual solution. No moving parts are present and less care need be expended in keeping the instrument in working order. One disadvantage of the gravimetric approach is, perhaps, that it does not enable the continuous addition of titrant to be performed when the reaction is sufficiently fast to permit the use of this type of procedure. However, a quasi-continuous procedure with rapid gravimetric additions followed by reading of the mass and potential without any stability test is being evaluated for use in routine determinations.

Finally, more complex titration procedures requiring the addition of more than one reagent, back-titrations and multiple standard additions (as are necessary for the generalized standard additions methods[11]) can be carried out by using the proposed gravimetric burette driven by the appropriate software. These applications of the gravimetric burette in routine laboratory tasks will be described in a subsequent paper.

APPENDIX

LISTING 1 Main QUICKBASIC 4.5 Sub-programs to Control the Gravimetric Burette

```
' The following constant values associated with the
' interface control and addresses of the devices
' should be declared in the main module of the program.
' The following sub-programs assume that the user card has
' been initialized and that the asynchronous interface is in
' step. For details of the interface and user card operation
' see refs. 6–8.

CONST contr% = 1003, pa% = 1000, pb% = 1001, pc% = 1002

CONST ohstr% = 3, olstr% = 2, ihstr% = 5, ilstr% = 4

CONST iack% = 32, oack% = 128, hill% = 255

CONST adc% = 254, dac% = 253, vadd% = 251, senadd% = 247

CONST iof% = 1        ' enables/disables 1/0, 1 = enabled,
                      ' 0 = disabled

CONST tmax = 400      ' time in seconds necessary to empty a
                      ' full burette flask

COMMON SHARED dout%,ma,stb

' initialization of the user card (see ref. 7)
```

```
OUT contr%,193: OUT pa%,hill%: OUT pb%,ohstr%

' the following sub-programs are necessary to control the
' gravimetric
' burette and to perform analytical procedures


SUB fillburette(n%,ma)              ' fill the burette n% (1<n%<4)

    empty% = 2 (n%-1)
       nr% = n% + 3

   CALL readinter(247,di%)          ' checks for level sensor state
      IF (di% AND empty%) = 0 THEN GOSUB fill : EXIT SUB
' flask is empty
         CALL valveon(n%)           ' flask is being emptied
                                    ' flask is not empty
   WHILE (di% AND empty%) > 0       ' waiting for an empty flask
      CALL readinter(247,di%)
   WEND
      CALL valveoff(n%)
       GOSUB fill
   EXIT SUB

 fill:
       CALL readbalance(flaginst%,mass,stb)
        mi=mass


          CALL valveon(nr%)
       WHILE ABS(mass-mi) < ma
       CALL readbalance(flaginst%,mass,stb)
       WEND
          CALL valveoff(nr%)
 RETURN

END SUB

SUB addtime(n%,t,madd)    ' delivers solution from burette n%
                          ' during the
                          ' time interval t (s). Returns madd,
                          ' the true added mass
      told = t
   IF t > tmax THEN EXIT SUB
   CALL readbalance(flaginst%,mass,stb)
    mi = mass: maddi = 0
    empty% = 2 (n%-1): ti=TIMER
    CALL valveon(n%)
   WHILE (TIMER - ti) < t
      CALL readinter(247,di%)
       IF di% AND empty% = 0 THEN
        CALL valveoff(n%)
        CALL readbalance(flaginst%,mass, stb)
        maddi = ABS(mass - mi)
             dt = TIMER - ti: t = t - dt
        CALL fillburette(n%,ma%)
        CALL readbalance(flaginst%,mass,stb)
        mi = mass
            ti = TIMER
        CALL valveon(n%)
       END IF
   WEND
      CALL valveoff(n%)
      CALL readbalance(flaginst%,mass,stb)
      madd = maddi + ABS(mass - mi)
        t = told
END SUB

SUB addmass(n%,m,madd)               ' adds solution from burette n%
                                     ' until the mass m is
                                     ' approximately added. Returns
                                     ' madd, the true mass added
```

```
            mold = m
        IF m > ma% THEN EXIT SUB
          CALL readbalance (flaginst%,mass,stb)
          mi = mass: empty% = 2 (n%-1): maddi = 0
          CALL valveon(n%)
    WHILE ABS(mass - mi) < m
          CALL readinter(247,di%)
          CALL readbalance(flaginst%,mass,stb)
      IF di% AND empty% = 0 THEN
          CALL valveoff(n%)
          CALL readbalance(flaginst%,mass,stb)
            maddi = ABS(mass-mi): m = m - maddi
          CALL fillburette(n%,ma%)
          CALL readbalance(flaginst%,mass,stb)
            mi = mass
          CALL valveon(n%)
      ENDIF
    WEND
          CALL valveoff(n%)
          CALL readbalance(flaginst%,mass,stb)
          madd = maddi + ABS(mass - mi)
            m = mold
END SUB


SUB readbalance(flaginst%,mass,stb)      ' reads the balance
                                         ' through RS232 in COM2
        IF iof% = 0 THEN EXIT SUB

            OPEN "COM2: 9600,N,7,2,RS,DSO" FOR INPUT AS #1
            n=0: mass1=0: mass2= 2*stb

DO UNTIL n > 10 OR ABS(mass2 - mass1) =< stb
            GOSUB readmass
             mass1 = mass

            GOSUB readmass
             mass2 = mass
            n=n+1
LOOP
        IF n > 10 then flaginst% = 1 ELSE IF n =< 10 THEN
flaginst% = 0
        dout% = dout% and 191
        CALL outda(251,do%)
        CLOSE #1

EXIT SUB

  readmass:
        INPUT #1, mass$
        mass = VAL(mass$)
  RETURN

END SUB


SUB valveon(nv%)                        ' turns the valve nv% on
        IF nv%>6 OR nv%<1 THEN EXIT SUB
        dout% = dout% OR (2 (nv%-1))
    CALL outda(251,dout%)
END SUB


SUB valveoff(nv%)             ' turns the valve nv% off
        IF nv% > 6 OR nv% < 1 THEN EXIT SUB
        dout% = dout% AND (255-(2 (nv%-1)))
        CALL outda(251,dout%)
END SUB


SUB outda(ad%,bytetosend%)              ' used for output data to
                                        ' the interface
```

```
    IF iof% = 0 THEN EXIT SUB
      OUT pb%,ohstr%
          OUT pa%,ad%
        OUT pb%,olstr%
    WHILE (INP(pc%) AND oack% = 0) : WEND
        OUT pb%,ohstr%
      OUT pa%,bytetosend%
        OUT pb%,olstr%
    WHILE (INP(pc%) AND oack% = 0) : WEND
        OUT pb%,ohstr%
      OUT pa%,hil%
END SUB


SUB readinter(ad%,di%)               ' for input data from the
                                     ' interface. This sub-program
                                     ' can access the sensor state
                                     ' and the ADC converted value
    IF iof% = 0 THEN EXIT SUB
    OUT pb%,ohstr%
        OUT pa%,ad%
      OUT pb%,olstr%
      WHILE (INP(pc%) AND oack%) = 0: WEND
      OUT pb%,ohstr%
          OUT pb%,ihstr%
        OUT pb%,ilstr%
    WHILE (INP(pc%) AND iack%) = 0: WEND
        di% = INP(pa%)
END SUB
```

References

1 Tamberg, T., *Fresenius' Z. Anal. Chem.*, 1978, **291**, 124.
2 Luft, L., *Talanta*, 1980, **27**, 221.
3 Kratochvil, B., and Nolan, J. E., *Anal. Chem.*, 1984, **56**, 586.
4 Chipperfield, J. R., and Webster, D. E., *Anal. Chim. Acta*, 1987, **197**, 373.
5 Mak, W. C., and Tse, R. S., *J. Chem. Educ.*, 1991, **68**, A95.
6 Souza, P. S., and Pasquini, C., *Lab. Micro*, 1990, **9**, 77.
7 Malcolme-Lawes, D. J., *Lab. Micro.*, 1987, **6**, 16.
8 Malcolme-Lawes, D. J., *Lab. Micro.*, 1987, **6**, 122.
9 Horowitz, P., and Hill, W., *The Art of Electronics*, Cambridge University Press, Cambridge, 8th edn., 1987.
10 Eckshlager, K., *Errors, Measurements and Results in Chemical Analysis*, Van Nostrand Reinhold, London, 1972, p. 144.
11 Saxberg, B. E. H., and Kowalski, B. R., *Anal. Chem.*, 1979, **51**, 1031.

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