CHROM. 14,639

COMPUTERIZED AUTO-CONTROL OF ON-LINE PROCESSES OR LABORATORY GAS AND LIQUID CHROMATOGRAPHS

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SUMMARY

The deferred standard concept can help the operator in controlling on-line the reliability of any process or laboratory gas or liquid chromatographic apparatus. However, more sophisticated auto-control of the chromatograph can be achieved by computerizing the interpretation of some chromatographic quantities for the deferred standard such as peak area, peak height and retention time, and can discriminate among the sample injection, the separation or the detection systems as sources of problems. This approach has been made possible owing to a commercial computing integrator which, in addition to quantitative information, displays messages about the status of the chromatograph.

This permanent auto-control suggests what the control unit of a modern process gas or liquid chromatograph, which has to be included in a closed loop control, should be.

INTRODUCTION

The concept of the deferred standard which has been published several times[1–4] has already succeeded in the on-line measurement of process chromatograph reliability and could be a real enhancement for both gas and liquid chromatographs, especially with the advent of microprocessors as control units of process or laboratory chromatographs used in routine control.

The deferred standard has three capabilities: alarm, calibration and maintenance functions. The purpose of this paper is to show how the first aspect, the alarm function, can be emphasized by using a microprocessor and what a future process gas or liquid chromatograph might look like.

DEFERRED STANDARD CONCEPT

The deferred standard (D.S.) is a pure compound, injected in each analytical sequence, the injection of which is deferred or delayed with respect to the injection of the sample to be analysed in such a way that the deferred standard elutes within the analysis time of the sample, but without interfering with any component of the mixture (Fig. 1).
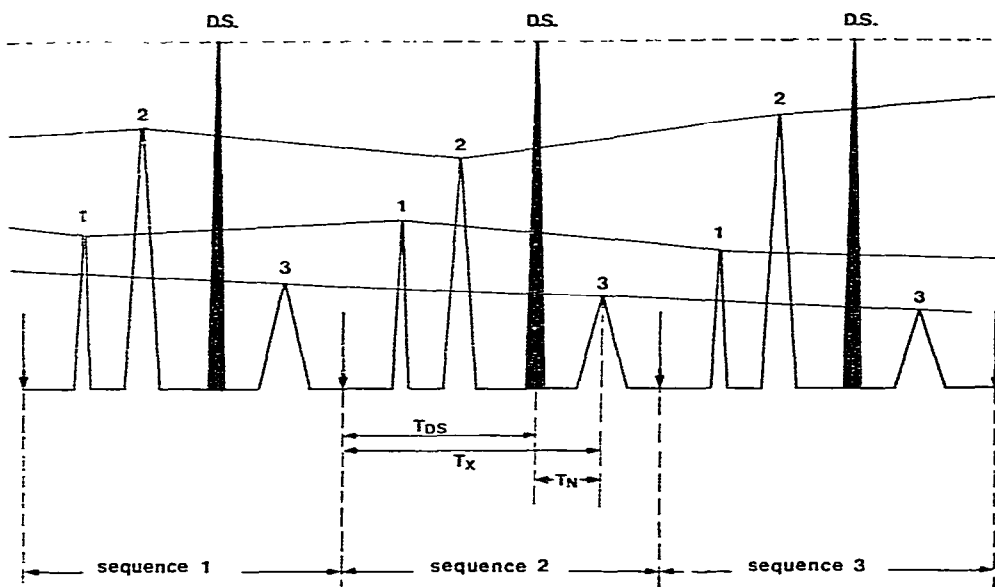
Fig. 1. Continuous checking of the reliability of a process chromatograph by the deferred standard concept.

As an alarm function, the reproducibility of the D.S. peak from one injection to the next indicates the good working order of the chromatograph, and the quantitative results for the sample to be analysed can be taken into account with confidence in the process control. In addition, this continuous checking of the reliability of the process chromatograph allows the plant operator to discriminate immediately between the analyser or the chemical process in cases of failure.

EXPERIMENTAL

This work was carried out with commercial equipment including, a Carlo Erba Model GT laboratory chromatograph automated with Spectra-Physics 4100 a computing integrator which offers, for the first time in this kind of appliance, part of the RAM memory to be programmed in modern computer language by the user himself. The interface between the chromatograph and the computing integrator was a home-made device, set up for the control of automatic injection, switching valves of the chromatographic circuit and different solenoid valves of the sampling line.

The equipment was installed on-line in a pilot plant for the continuous measurement of hydrogen in a chemical process. The chromatographic conditions were limited to a molecular-sieve column fed with argon as the carrier gas. For accuracy in quantitative measurements, pure hydrogen was choosen as the D.S., and was injected through the same injection valve as the process sample. Both the sample and the hydrogen D.S. were fed alternatively through a three-way solenoid valve and equilibrated at atmospheric pressure for 30 sec before injection.

Fig. 2 is a schematic diagram of the sampling and chromatographic circuits.
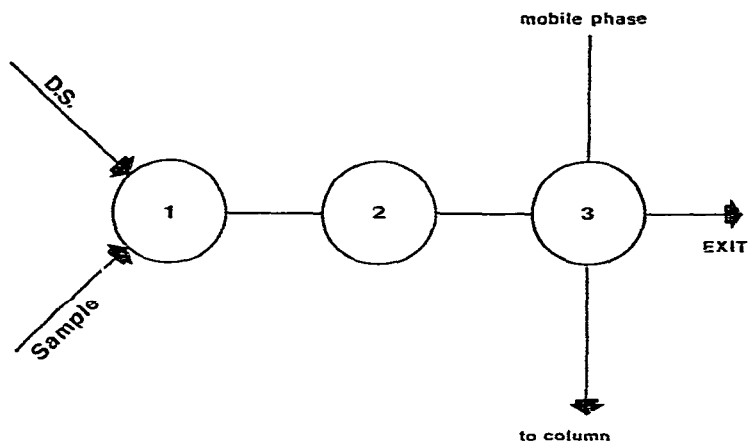
Fig. 2. Schematic diagram of sample and deferred standard circuits. 1 = Selector valve; 2 = stop-valve (atmospheric pressure); 3 = injection valve.

Primary alarm function of the deferred standard

For quantitative measurements, in which the peak area is linked to the amount of injected solute, the D.S. peak area rather than peak height is chosen as the most suitable parameter to trigger off an alarm when the value exceeds upper and lower fixed limits. These limits for the D.S. peak area are set first according to the standard deviation of the D.S. peak repeatability and second according to the requirements of the accuracy of quantitative measurements of solutes with regard to the D.S. peak.

The continuous checking of the peak area of the D.S. provides invaluable information about the overall status of the process gas chromatograph, but this permanent auto-control may be more sophisticated in order to make easier the diagnostic of any chromatographic failure and decrease the cost of maintenance.

Secondary alarm function of the deferred standard

By computerizing parameters of the D.S. peak such as peak area, peak height and retention time, discrimination between the detection, the injection and the separation systems as possible sources of problems is now possible and could be very helpful to the chromatographer searching for a malfunction or a failure of the process chromatograph. In addition to the main functions of an ordinary control unit of either a PGC and PLC, *i.e.*, timing of the analysis and chromatographic data reduction, the Spectra-Physics 4100 computing integrator also carried out the auto-control of the chromatograph and in this way acted as a modern control unit for both the PGC and the PLC.

Fig. 3 shows the algorithm built up on the three parameters peak area, peak height and retention time of the D.S. peak for failure diagnosis. The D.S. is logically identified by the absolute time from the beginning of the sample run to its peak maximum, as this deferred injection is ignored by the SP 4100. This time ($T_{D.S.}$) must be within a certain range specified by the operator; if it is outside the specified limits a "D.S. not found" message is displayed.

The next parameter checked is the peak area (S) and the peak height (H) of the

D.S. As previously pointed out, peak area depends on detection conditions, whereas peak height is related mainly to the injection conditions. To make the retention parameter more sensitive to chromatographic variations (carrier gas flow-rate,
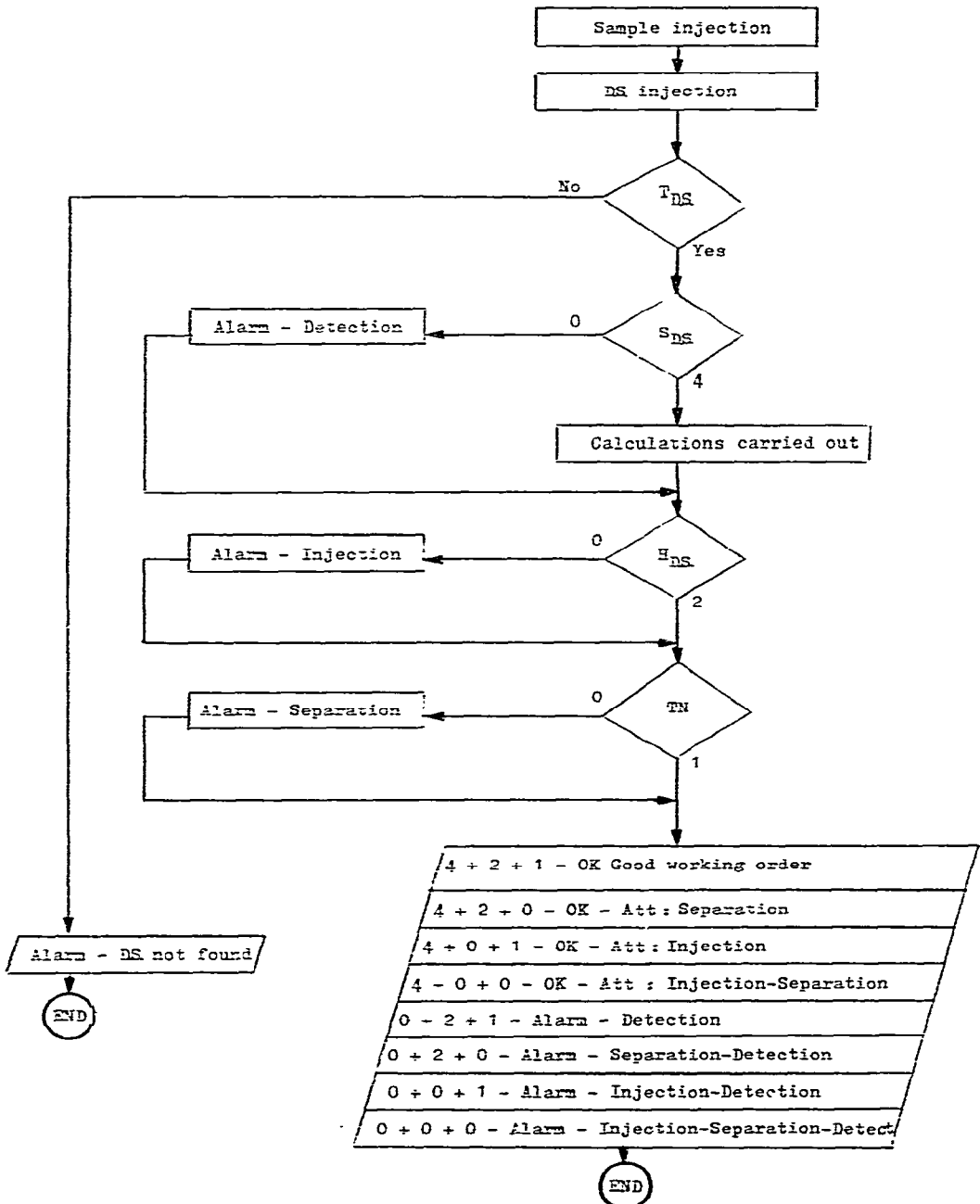

Fig. 3. Algorithm of the alarm function of the deferred standard.

column temperature, etc.), the selection of the difference in retention times between the D.S. peak and a reference peak has been chosen:

$$TN = | \ T_X - T_{D.S.} |$$ (1)

where TN is the difference between the absolute retention times as shown in Fig. 1 and T_X and $T_{D.S.}$ are the absolute retention times of peak X and D.S., respectively.

Any peak in the chromatogram may be a reference peak provided that it is always present in the sample. However, the larger the retention time of the reference peak the more sensitive it is to fluctuations in the operating conditions.

Limiting values of these parameters ($T_{D.S.}$, S, H and TN) are entered via a Basic dialogue before starting the routine analysis. To make the trouble-shooting software more understandable, values 1 and 0 have been attributed to these parameters when they are inside or outside their limits, respectively. Table I gives the various logical cases encountered when variations of these three parameters occur.

The meaning of possible variations occurring in the D.S. peak area may be some change or drift in the detector operating conditions, *i.e.*, variation of the d.c. current or block temperature for a thermal conductivity detector or variation of the flame temperature for a flame ionisation detector owing to changes in the flow-rate. Another meaning of increases in the D.S. peak area could be an unexpected peak eluting close to and interfering with the D.S. peak. In this case the D.S. injection must be delayed further so that the D.S. peak elutes at a suitable position not subject to interferences.

If the D.S. peak height is outside the specified limits, the injection function is first involved: the causes of this failure may be blockage of the injection valve, malfunction of the pneumatic actuator owing to a lack of air pressure or variation of the vaporization temperature in the case of a liquid sampling valve for PGC. Also, variation of the temperature of a gas sampling valve may cause enlargement of the peak owing to diffusion of the solute when the volumetric flow-rate of the carrier gas fluctuates. For instance, Table II and Fig. 4, show the effect on the peak height of a lack of air pressure in the actuator of a commercial liquid sampling valve for PGC. As the injection is not sufficiently instantaneous when the air pressure varies, the peak height is affected while the peak area remains constant. Halving the air pressure leads to a decrease of 13 % in the peak height and 0.8 % in the peak area.

Variation of TN means that some alterations in the separation conditions (column temperature, mobile phase flow-rate, elution of stationary phase, etc.) have occurred. Considering the peak area, S, the remarks made about the primary alarm function also apply here.

To illustrate the Basic program for the Spectra-Physics 4100 computing integrator. some examples are given below.

The procedure based on a conversational dialogue is as follows. Entry of PH = 1 on the SP 4100 before starting a run makes a report on peak heights while peak areas are stored. Afterwards an additional report on peak areas is obtainable for those peaks in peak storage by entering PH = 2 and pressing the REPRT key.

Entry of RUN initiates a special dialogue (see Fig. 5). The program asks for the name of the analysis, then the number of the D.S. peak as the SP 4100 identifies peaks by chronologic figures. Quantitative calculations need the D.S. concentration to be entered. Then the "windows" (limits) are requested for peak area, peak height and

TABLE I

TROUBLE-SHOOTING DIAGNOSTIC

Deferred standard parameter				Actions
$T_{D.S.}$	H	TN	S	
0				*Alarm:* D.S. not found. No calculation of component concentrations
1	1	1	1	Good working order. Calculation of component concentrations carried out with respect to D.S.
1	0	1	1	Calculations carried out with respect to D.S. Care of injection system
1	0	0	1	Calculations carried out with respect to D.S. Care of injection and separation systems
1	1	0	1	Calculations carried out with respect to D.S. Care of separation system
1	1	1	0	*Alarm:* No calculations reported. Care of detection system
1	1	0	0	*Alarm:* No calculations reported. Care of detection and separation systems
1	0	1	0	*Alarm:* No calculations reported. Care of detection and injection systems
1	0	0	0	*Alarm:* No calculations reported. Care of detection, separation and injection systems

retention time of the D.S. peaks, labelled as Max S, Min S, Max $T_{D.S.}$ and Min $T_{D.S.}$. A reference peak number has to be entered with the upper and lower values of TN as defined previously. Each peak whose concentration is to be calculated with respect to the D.S. peak has its number entered, then its relative response factor and name. To end the dialogue, the letter E (for END) is entered.

TABLE II

EFFECT OF VARIATIONS IN AIR PRESSURE IN THE ACTUATOR OF A PROCESS LIQUID SAMPLING VALVE ON PEAK AREAS AND PEAK HEIGHTS

Injection of 1 μl of carbon tetrachloride. Injection frequency: every 10 min. Vaporization temperature: 120°C. Peak areas and peak heights measured by computer.

Number of injections	Air pressure on valve actuator (bar)	Peak area			Peak height		
		S (average of last 10 runs)	σ	Difference from previous measurement (%)	H (average of last 10 runs)	σ	Difference from previous measurement (%)
3168	6	2655	0.009	—	15.76	0.15	—
5184	3	2676	0.008	0.8	13.90	0.3	13.4
5760	4	2679	0.009	0.1	14.40	0.1	3.5

Queries and peak height and peak area reports are displayed in Fig. 5. Fig. 6 shows several messages displayed when the parameter "window" was changed artificially to test the program. Message A indicates that D.S. has not been found, as peak 4 does not exist in the chromatogram. Message B displays the calculated concentrations for peaks X1 and X2, the values of the checked parameters, the chromatographic quantities of the D.S. and reference peaks and finally the status of the alarm function.
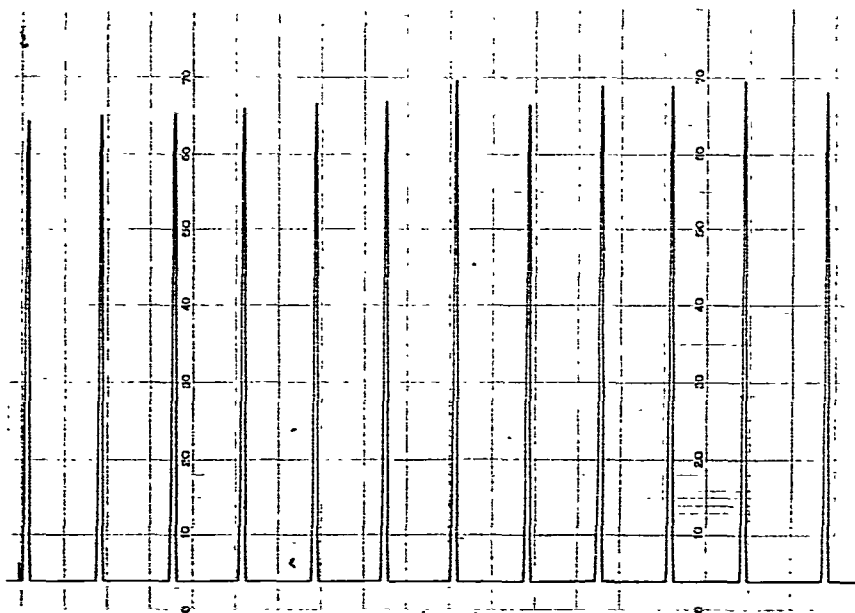

Fig. 4. Effect on peak shape of variation of air pressure in the pneumatic actuator of an automatic liquid sampling valve for a process gas chromatograph.

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RUN
DEFERRED STANDARD - ALARM AND CALIBRATION FUNCTIONS

ANALYSE: X
PIC DS 2
Conc DS 100
MAX S DS 25000
MIN S DS 22000
MAX H DS 7000
MIN H DS 5000
MAX T DS 40
MIN T DS 33
PIC REF 2
MAX TN 17
MIN TN 13
No PIC 1
RF .5
NAME X1
No PIC 3
PF .25
NAME X2
No PIC F
END OF DIALOG
```

PH=1

```
                              00:25:49

FILE 1      METHOD  0.      RUN    4      INDEX   4

PEAK#        HT%          RT      PK HT  BC

    1        51.16        28.      12467 02
    2        28.267       36.       6888 02
    3        20.573       51.       5013 03

TOTAL       100.                  24363
```

PH=2

```
                              30:25:49

FILE 1      METHOD  0.      RUN    4      INDEX   4

PEAK#       AREA%         RT      AREA  BC

    1        38.302       28.      31954 02
    2        28.693       36.      23937 02
    3        33.004       51.      27534 03

TOTAL       100.                  83425
```
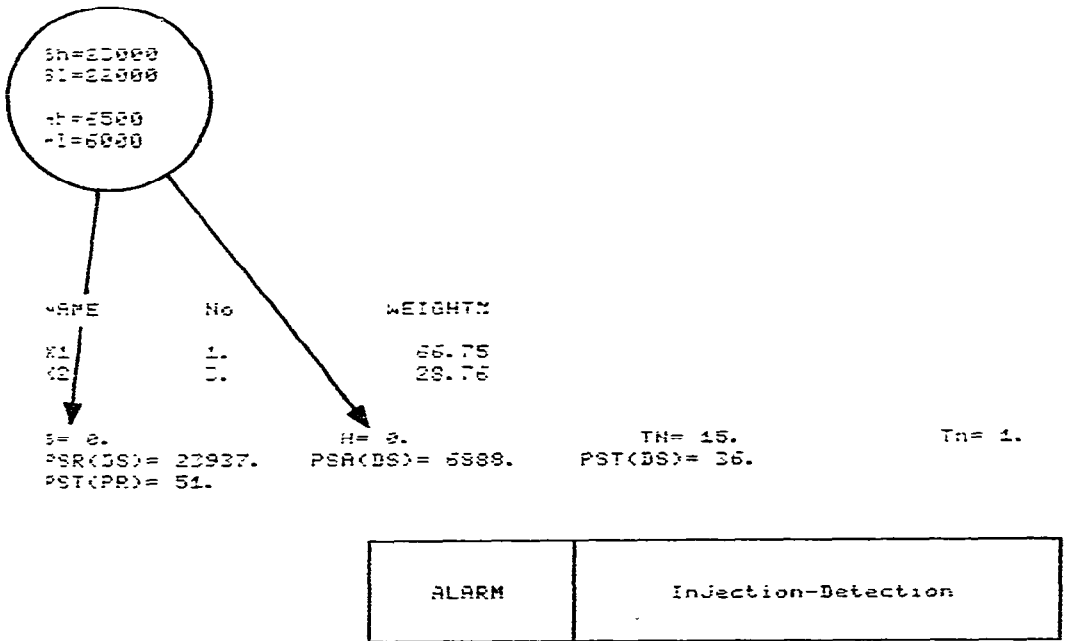
Fig. 5. Queries for the alarm function of the deferred standard.

Concentrations are calculated according to the following well known equation:

$$C_X = C_{D.S.} \cdot f_{X/D.S.} \cdot \frac{A_X}{A_{DS}} \tag{2}$$

where C_X is the concentration of solute X, $C_{D.S.}$ is the concentration of D.S., $f_{X/D.S.}$ is the relative response factor of solute X with respect to D.S., expressed in volume or weight units, and A_X and $A_{D.S.}$ are the peak areas of solute X and D.S., respectively.

To make the Basic program simpler and more elegant, a contrivance has been introduced: instead of values of 1 and 0 occording to the status of the parameters, values of 4 or 0 are now attributed to S, 2 or 0 to H and 1 or 0 to TN, written with the

A

DS = 4

ALARM	D.S. NOT FOUND

B

NAME	No	WEIGHT%
X1	1.	56.75
X2	3.	28.76

S= 4.   H= 2.   TN= 15.   Tn= 1.
PSR(DS)= 23937.   PSR(DS)= 6888.   PST(DS)= 36.
PST(PR)= 51.

O K	GOOD WORKING ORDER

Fig. 6. Examples of displayed messages (checked parameters varied artificially, see text).
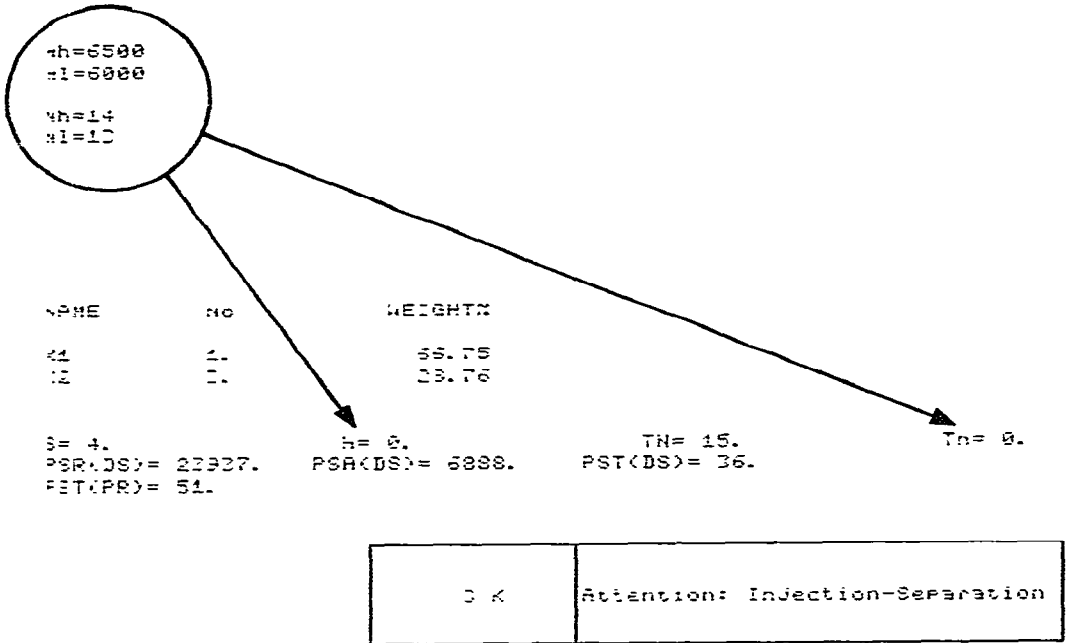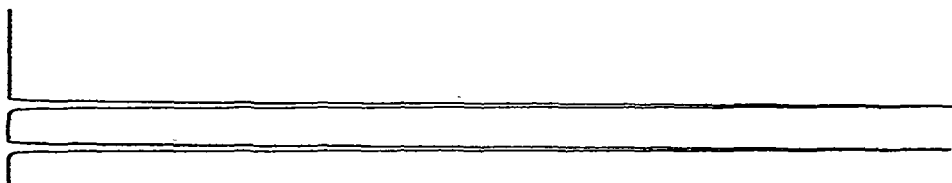
Fig. 7. Examples of reports and messages.

INJECT TIME 511:26:02

```
NOM          No              POIDS %

H2           2.              96.17


S= 4.                  H= 2.                    TN= 49.              Tn= 1.
PSR(DS)= 3757296.  PSA(DS)= 576368.   PST(DS)= 113.
PST(PR)= 162.
```
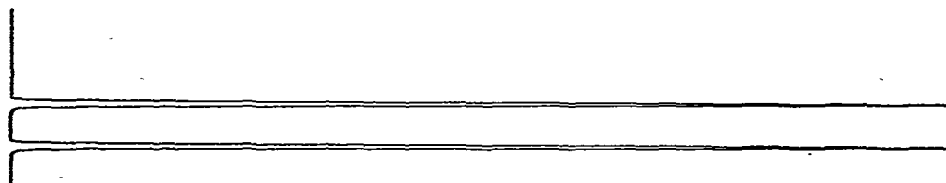
O K	TOUT VA BIEN

INJECT TIME 511:41:02

```
NOM          No              POIDS %

H2     .     2.              96.37


S= 4.                  H= 2.                    TN= 58.              Tn= 1.
PSR(DS)= 3756651.  PSA(DS)= 575957.33PST(DS)= 113.
PST(PR)= 163.
```
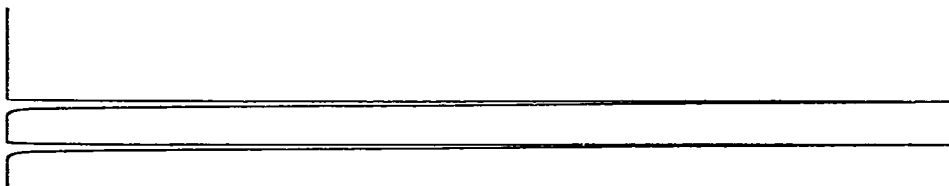
O K	TOUT VA BIEN

Fig. 8.

INJECT TIME   511:56:02

NOM   No   POIDS %

H2   2.   96.38

S= 4.   H= 2.   TN= 50.   Tn= 1.
PSR(DS)= 3762879. PSA(DS)= 570462.67PST(DS)= 112.
PST(PR)= 162.

O K	TOUT VA BIEN

INJECT TIME   512:11:03

NOM   No   POIDS %

H2   2.   95.38

S= 4.   H= 2.   TH= 50.   Tn= 1.
PSR(DS)= 3769894. PSA(DS)= 576013.33PST(DS)= 113.
PST(PR)= 163.

O K	TOUT VA BIEN

Fig. 8. Series of analytical sequences of an on-line chromatograph permanently checked with the deferred standard concept.

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LIST

   10 :"DEFERRED STANDARD - ALARM & CALIB FUNCTIONS": !
   20 INPUT "ANALYSIS ",An
   30 INPUT "PIC DS ",DS: INPUT "Conc DS ",Cd
   40 INPUT "MAX S DS ",Sh: INPUT "MIN S DS ",S1
   50 INPUT "MAX H DS ",Hh: INPUT "MIN H DS ",H1
   60 INPUT "MAX T DS ",Th: INPUT "MIN T DS ",T1
   70 INPUT "REF PIC "; PR
   80 INPUT "MAX TN ",Nh: INPUT "MIN TN ",N1
   90 I=1
  100 INPUT 'PIC No "; Ni(I)
  110 IF RXD <> 15 THEN 150
  120 INPUT "RF ",Fi(I)
  130 INPUT "NAME "; Nc(I)
  140 I=I+1: GOTO 100
  150 :"END OF DIALOG ": Nf=I-1: END: !!
  160 IF PST(DS))=Th OR PST(DS)<=T1 THEN 170 ELSE 200
  170 !!
  180 GRAPH 350,350,1: !:
  190 !" ALARM          D S NOT FOUND": GOTO 600
  200 !"NAME        No        WEIGHT %": !
  210 FOR I=1 TO Nf
  220 Ci(I)=Cd*Fi(I)*(PSR(Ni(I))/PSR(DS))
  230 ! $5.03 No(I); $10.3 Ni(I):TAB20 Ci(I)
  240 NEXT
  250 !!
  350 TN=PST(DS)-PST(PR)
  360 IF PSR(DS))=Sh OR PSR(DS)<=S1 THEN S=0 ELSE S=4
  370 IF PSR(DS))=Hh OR PSR(DS)<=H1 THEN H=0 ELSE H=2
  380 IF TN)=Nh OR TN<=N1 THEN Tn=0 ELSE Tn=1
  390 !"S=";S;TAB20"H=";H;TAB40"TN=";TN;TAB60"Tn=";Tn
  400 !"PSR(DS)=";PSR(DS);"PSA(DS)=";PSA(DS)
  410 !"PST(DS)=";PST(DS);"PST(PR)=";PST(PR)
  420 A1=S+H+Tn
  430 !: PLOT 0
  440 GRAPH 350,250,1: !:
  450 ON A1+1 GOTO 460,470,480,490,500,510,520,530
  460 !" ALARM       Injection-Separation-Detection": GOTO 600
  470 !" ALARM          Injection-Detection": GOTO 600
  480 !" ALARM          Separation-Detection": GOTO 600
  490 !" Alarm             Detection": GOTO 600
  500 !TAB3"O K       Attention: Injection-Separation": GOTO 600
  510 !TAB3"O K          Attention: Injection": GOTO 600
  520 !TAB3"O K          Attention: Separation": GOTO 600
  530 !TAB3"O K          GOOD WORKING ORDER": GOTO 600
  600 RESTORE 620: FOR I=1 TO 7 : READ X,Y,Z
  610 GRAPH X,Y,Z: NEXT : !&: ECHO1
  620 DATA 0,300,1,500,300,0,500,950,0,0,950,0,0,300,0
  630 DATA 0,495,1,500,495,0
  640 PLOT AUTO
  650 END
 2088 S=#C300: K=#C300: INPUT "LINE ?" L: LIST(L)
 2089 I=2S+2PEEK(PEEK#C2A2+S): FOR T=S TO S+64
 2090 IF C<>13 THEN I=I+1: C=PEEK I AND #7F: POKE I,C
 2091 NEXT : POKE K,0,0,5: END
 3020 D=DT: IF D<T1 THEN D=T1 ALWAYS IF MN=0 THEN 5200
 4850 POKE #C2CD,0: DISP : GOTO 160: END
```

Fig. 9. Basic program for use with the SP 4100.

Tn label. *PSR* (D.S.), *PSA* (D.S.) and *PST* (D.S.) are the SP 4100 parameters indexed in order of detection for peak area, peak height and retention time of the D.S. peak, respectively, to access the peak storage in the core memory of the computing integrator. In the same way *PSR* (PR) is the retention time of the reference peak. All of this information is displayed in the second part of message B.

On the other hand, the first part of the framed message gives the overall status of the process chromatograph, and the second part displays the secondary alarm or diagnosis.

As can be seen in Fig. 5 or 6, the normal SP 4100 report, which is no longer useful, has been suppressed through the Basic software (see below).

Fig. 7 shows two more reports and messages in which some windows have been changed, as indicated on the left-hand side of the report, with the corresponding message.

Finally, a series of analytical sequences, reports and messages for the measurement of hydrogen in the pilot-plant process are given in Fig. 8. Reading the analytical bulletins, the plant operator and/or the control computer of the unit takes the successive calculated concentrations of hydrogen as valid and reliable for controlling the process, as the status of the on-line chromatograph remains in "good working order".

It is obvious than a more detailed and precise diagnosis might be developed to increase further the capabilities of the alarm function of the D.S. concept. For instance, in addition to the previous parameters, peak asymmetry, peak shape, etc., may reveal more about the performances of the different parts of the chromatograph.

The D.S. Basic program for use with the SP 4100, is given in Fig. 9. It should be noted that after obtaining any D.S. chromatographic quantities required for answering the program dialogue, the own SP 4100 report is no longer necessary and can be suppressed. Line 3020 of the program has to be modified as follows: instead of the number 5200 which ends the line, put 4850, as shown in the program in Fig. 9.

CONCLUSION

It is obvious that the recent advent of microprocessors in analytical instrumentation makes the operator's task easier. However, the real improvement seems to lie in the portion of the computer core memory which has been devoted to the operator for various programs or for subsequent calculations. This trend should be encouraged for the benefit of both the technique and the operator, the technique because it increases the capabilities of the apparatus and the operator because it enhances the status of his work.

The alliance of the deferred standard concept and the microprocessor is a good example of such a trend, particularly with on-line process GC or LC apparatus. On-line checking with a deferred standard, allowing any process chromatograph to fit the main criteria of process monitors (reliability, credibility and low maintenance), should allow the process gas or liquid chromatograph to be included in a closed-loop control with more confidence.

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