NWRI CONTRIBUTION 89-84

INSTRUCTION MANUAL FOR DETERMINATION OF Ca AND Mg by FLOW INJECTION ANALYSIS AND ATOMIC ABSORPTION SPECTROSCOPY

by

I. Sekerka and J.F. Lechner[1]

Analytical Chemistry Project
Research and Applications Branch
National Water Research Institute
867 Lakeshore Road, P.O. Box 5050
Burlington, Ontario L7R 4A6

January 1989

MANAGEMENT PERSPECTIVE

This report is intended to aid the client (NWQL) and prospective users of Flow Injection Technology (FIA). It is an instruction manual for the application of FIA in conjunction with AAS for the automated determination of Ca and Mg by Atomic Absorption Spectroscopy. With a throughput rate of 120 to 180 samples/h, high accuracy and low detection limits, the described method is superior to commonly used direct aspiration AAS procedures. It meets the requirements of NWQL for precision and accuracy, while speeding up analysis by a factor of 2 to 3, which are important aspects for a routine environmental analytical laboratory.

Dr. J. Lawrence
Director
Research and Applications Branch

PERSPECTIVE - GESTION

Ce rapport est destiné au client (LNQE) et aux utilisateurs éventuels de la technologie d'injection par flux. Il s'agit d'un manuel de l'utilisateur expliquant l'application de la technologie d'injection par flux au dosage automatique du Ca et du Mg par spectrophotométrie d'absorption atomique. Avec un rendement de 120 à 180 échantillons/heure, une bonne précision et des limites de détection à un niveau bas, la méthode décrite est supérieure aux méthodes usitées de spectrophotométrie d'absorption atomique par aspiration directe. Cette méthode répond aux exigences de précision et d'exactitude du LNQE et accélère les dosages par un facteur de 2 à 3; ce sont là des aspects importants du travail routinier qui est exécuté dans les laboratoires d'analyse environnementale.

Dr J. Lawrence
Directeur
Direction de la recherche et des applications

ABSTRACT

Flow Injection Technology is applied to Atomic Absorption Spectroscopy for automated Ca and Mg analysis. A rate of 120-180 samples per hour is optimal. Sample volume requirements are from 500 to 1000 μL per analysis. Analysis precision is less than 2% RSD. Detection limits are well within acceptable values for Ca and Mg by AA spectroscopy. The described method of FIA controlled AA operation is superior to direct aspiration AA procedures.

RÉSUMÉ

La technologie d'injection par flux est appliquée à la spectrophotométrie d'absorption atomique pour le dosage automatique du Ca et du Mg. Une cadence de traitement des échantillons de 120 à 180 échantillons/heure est optimale. Il faut en volume 500 à 1000 uL d'échantillon pour chaque dosage. La précision du dosage est supérieure à 2 % RSD. Les limites de détection sont bien à l'intérieur des valeurs acceptables de dosage du Ca et du Mg par spectrophotométrie d'aborption atomique. La méthode d'absorption atomique à injection par flux décrite ici est supérieure aux méthodes par aspiration directe.

1.0 INTRODUCTION

Flow Injection Analysis (FIA), has been adapted for automated sample delivery in Atomic Absorption Spectroscopy (AA). It entails automated insertions of discrete (500 to 1000 µL) volumes of sample, depending on the loop size, into a constantly flowing lanthanum reagent stream, which is directly pumped into the nebulizer. This allows Ca and Mg analysis with high precision (less than 2% RSD) and low detection limits at speeds of 120 to 180 samples per hour. The introduction of a FIATRON microprocessor controlled FIA valve and LABTRONIC DP 1000 Data Logging System has enhanced the advantages of FIA controlled AA operation.

2.0 APPARATUS

A block diagram of the system is shown in Fig. 1. The equipment consists of a Perkin Elmer Model 403 AA Spectrophotometer, interfaced to a FIATRON FIA-Valve 2000. An ISIS autosampler including four LAB PUMP JR. pumps, Model RHSY by Fluid Metering Inc. and a LABTRONIC DP 1000 Data Handling System.

3.0 REAGENTS

1. Lanthanum chloride stock solution (5% La). Weigh out 58.6 g lanthanum oxide (La_2O_3) and transfer to a 1000 mL beaker. Add about 500 mL deionized water, followed by 100 mL concentrated HCL. Heat and stir the mixture until the salt dissolves. Cool, filter into a 1000 mL flask and make up to mark with deionized water.
2. Lanthanum chloride working solution (1% La). Prepare by diluting the lanthanum chloride stock solution by a factor of 1:5 with deionized water.
3. Stock calcium and magnesium solutions. See Water Quality Methods Manual for instructions on preparation of the solutions.

4. Deionized water for carrier (c) and wash (w). The recommended lanthanum solution concentration has been reduced thereby increasing operating time of the burner to at least four hours, without having to worry about premature lanthanum buildup around the burner slots.

4.0 SYSTEM ASSEMBLY

The FIA manifold is assembled according to Fig. 1 and 2. Connections to the valve are made via silicone rubber tubing connectors. All tubing connections between the pump, the sampler, the valve unit and the nebulizer should be kept to a minimum to prevent zone spreading. Also, carefully read all operating manuals and the appendix section of this manual.

5.0 OPTIMIZATION OF THE METHOD

For successful operation of FIA controlled AA spectroscopy, the AA operation must be optimized, as described in the Perkin Elmer Manual. See also in the Appendix - "Flow Injection System", "Changes in AA operation due to FIA interface", and "Quick Programming Instructions for FIATRON FIA Valve 2000". The following description applies to both modes of operating - "FIA with wash cycle" and "FIA without wash cycle" (Quick Programming Instruction for the FIATRON FIA Valve 2000).

In essence, what needs to be controlled is the time which the sample plug requires to travel from the sampler cup to the sample loop, and to fill the sample loop in the "Loading Cycle". It is the time it takes for the full content of the sample loop to be injected into the reagent stream in the "Injecting Cycle". Furthermore, consideration must be given to the "Wash Cycle", which introduces a wash plug, bracketed by two air plugs, and which are also in the path between sample and the sample loop, effectively separating the individual sample plugs. The timing has to be such that neither the air nor the wash are in the

sample loop during the injecting cycle. This is easily tested by observing the lead bubbles as the sampler begins the wash cycle. The wash cycle coincides with the inject cycle. As the sample loop injects its content into the reagent stream, the first air plug travels towards it, followed by the wash and the second air plug. But before the three plugs get to the loop, the valve must switch back to load. The three plugs must be allowed to pass through the loop and out into waste, before the next inject can be activated. The sample, once it is injected into the reagent stream, continues towards the nebulizer. The precise timing of the load and inject/wash cycles is extremely important for optimum performance.

6.0 OPERATION

Allow at least ten minutes for instrument warmup and stabilization. Assuming the FIA part of the system has been assembled according to instructions given in the Appendix and the AA spectrophotometer has been set and tuned to the parameter at hand, the nebulizer is connected to the FIA unit via the aspirator tubing and a number of test solutions are run through the system. The AA unit (nebulizer, flame, burner and settings), are optimized for the concentration ranges that are expected and the pumps are set to run. The FIATRON 2000 is programmed in Mode 20 and the LABTRONICS DP1000 is booted and is in system mode.

It is now time to match the analog AA output to the DP1000 input board. This may be accomplished via a D.C. amplifier like the NEFF Type 122 with variable input voltage and zero control features. Using the highest standard, set the analog input voltage from the detector to about 90% of the input voltage range chosen on the interface board of the DP1000. Then set the recorder range to 90% fullscale deflection. Once stability is assumed, start analysis by activating the data logging feature of the DP1000 and by starting the FIATRON 2000.

The sampler rack should contain an initializing sample, usually a standard, in its first position, followed by three blanks and a complete set of standards plus one reference standard in the upper range for drift correction. A few blanks are inserted after the standards, followed by the samples. Randomly insert a reference standard and a blank among the samples. End the run with a reference standard and a few blanks. When analysis is complete, save the raw data to disk.

At the end of the run, the system must be flushed by running distilled water through all tubing to remove lanthanum. The nebulizer must be disassembled and rinsed to prevent acid corrosion.

REFERENCES

1. Sekerka, I., Lechner, J.F. and Sandella G. Determinations of Ca and Mg by Term Injection Analysis and Atomic Absorption Spectroscopy. Manuscript No. 124-AMD-3-85-13.
2. Perkin-Elmer Model 403 AA Spectrometer Instructions Manual.
3. FIATRON FIA-Valve 2000 Instruction Manual.
4. LABTRONICS DP1000 Instruction Manual.
5. Karlberg, B. "Flow Injection Analysis" from Chemical Derivatization in Analytical Chemistry, Vol. 2. Edited by R.W. Frei and J.F. Lawrence, Plenum Publishing Corporation, 1982.
6. Ranger, C.B. Flow Injection Analysis. Analytical Chemistry, Vol. 53, No. 1 (1981).

APPENDIX

This part of the manual is intended to assist the operator in understanding the FIATRON Valve 2000 as it applies to AA operations. However, a more detailed explanation of FIA Principles may be obtained from the literature (ref. 5,6). Carefully read all manuals, especially the Operating Instructions of the FIATRON Valve 2000. The FIATRON Valve is essentially an 8-port valve, but is operated like the more conventional 6-port valve by installing a by-pass (see Fig. 3). It is important to realize that the sample in this system is aspirated through the valve into the sample loop, involving ports 6, 1, 4, and 5 in the "Load" position, and swept out into the reagent stream by the carrier during the "Inject" position involving ports 2,1,4, and 3. The sample loop is connected to ports 1 and 4 in Fig. 1 and 2.

The included schematics represent a block diagram of the system (Fig. 1). The flow injection system separate in Fig. 2 and the flow injection valve in the "Load" and "Inject" position in Fig. 3.

1. To program the FIATRON Valve 2000, see "Quick Programming Instructions" and the FIATRON Manual. To initialize programming of the unit, press STOP/START key and enter MODE 2 by pressing the MODE button and the number 20, then press ENTER and continue by pressing the NEXT LINE button. MODE 20 - MASTER will now appear on the screen. Continue by pressing the NEXT LINE button before each entry, followed by ENTER for each line entry. After the program is fully entered, press the STOP/START button and MODE 20 - MASTER will re-appear. You are now ready to begin analysis.

2. Make sure all reagent containers are filled and suction tubing is immersed.

3. Make sure all pump speeds are correct.

4. Drain bubbles out of the system by setting needle into wash and activate all pumps.

5. Make sure the recorder limits were set to 90% of the highest standard used in the run.

6. Before starting analysis, move sample tubes in auto-analyzer to start position.

7. Start analysis by pressing STOP/START button.

QUICK PROGRAMMING INSTRUCTIONS FOR FIATRON FIA VALVE 2000

1. FIA Without Wash Cycle

ENTER program as follows:

```
MODE 20
START SAMPLE = 1
SAMPLES  =  999
CYCLES/SMPL  =  1
SMPLS/CAL  =  1
CAL/SOLTNS  =  1
TS0  =  00 M 00 S
TS1  =  00 M 18 S
        VALVE POSITION = LOAD
        TTL 1-4 = OFF
        AUTO SMP = SMPL
TS2  =  00 M 12 S
        VALVE POSITION = INJ1
        TTL 1-4 = OFF
        AUTO SMP = NEXT
TS3 TO TS9 = 00 M 00 S
TS0 TO TC9 = 00 M 00 S
```

2. FIA With Wash Cycle Included

ENTER program as follows:

```
MODE 20
START SAMPLE = 1
SAMPLES  =  999
CYCLES/SMPL  =  1
SMPLS/CAL  =  1
CAL/SOLTNS  =  1
TS0  =  00 M 00 S
TS1  =  00 M 18 S
        VALVE POSITION = LOAD
        TTL 1-4 = OFF
        AUTO SMP = SMPL
TS2  =  00 M 10 S
        VALVE POSITION = INJ1
        TTL 1-4 = OFF
        AUTO SMP = WASH
TS3  =  00 M 01 S
        VALVE POSITION = INJ1
        TTL 1-4 = OFF
        AUTO SMP = NEXT
TS4  =  00 M 01 S
        VALVE POSITION = INJ1
        TTL 1-4 = OFF
        AUTO SMP = SMPLE
TS5 TO TS9 = 00 M 00 S
TS0 TO TC9 = 00 M 00 S
```

AA SETTINGS FOR Ca AND Mg FOR PERKIN ELMER 403 ATOMIC ABSORPTION SPECTROSCOPY

Parameter	Setting: Ca	Setting: Mg
Recorder Full Scale	.25 A	.5 A
Recorder Response	2 or 3	2 or 3
Slit	4	4
Wavelength	422.7 nm	285.2 nm
Oxidant Flow Rate	65 or 45*	65 or 45*
Fuel Flow Rate	45 or 30*	45 or 30*

Note: All analysis are done using the impact bead, air/acetylene flame, and the "Absorbance", "10 Average" and "Repeat" modes.

PUMPS:

The four pumps of the system are of type LAB PUMP JR, Model RHSY by Fluid Metering Inc. The following delivery rates are set individually.

"Carrier" Pump	(P3)	5.5 mL/min
"Sample" Pump	(P1)	10.0 mL/min
"Reagent" Pump	(P4)	1.5 mL/min
"Wash" Pump	(P2)	6.0 mL/min

Note: the pumps speed can be varied for optimum performance. But any change in pump speed may affect optimization of the system.

CHANGES IN AA OPERATION DUE TO THE FIA INTERFACE

1. The burner/nebulizer will be aspirating lanthanum at all times due to the continuous flow of reagent in the solution. Therefore the burner, aspirator and aspirator tubing may have to be cleaned more frequently than usual. Steadily decreasing peak heights may indicate a clogging problem.

2. The FIA system will add several feet of extra tubing between sample and the AA. This extra tubing will affect the rate of aspiration. Therefore, during preliminary adjustment of the lamp, burner and nebulizer, the test solubiotn should be aspirated through the running FIA system to get "optimum" adjustments. A constant stream of sample to the burner will be produced if the test sample is introduced via the carrier tubing. With the AA and pump running, put the suction end of the carrier pump into the beaker of the test solution and commence with the AA adjustments when the solution reaches the burner. The pump should be running at the recommended rate during these tests. The ISIS Autosampler must be on standby (wash) and the FIATRON 2000 in the "OFF" postion.

3. Increasing the pump speed increases the flow rate of liquid to the burner up to a maximum determined by the maximum rate of nebulization which in turn is determined by the oxidant flow rate. Increasing the pump speed beyond the maximum produces no change in signal magnitude (see AA, FIA, and miscellaneous settings for Ca and Mg in this manual). The overall flow-rate should be 7-8 mL/min. a flow-rate set too high may lead to leaking around the aspirator tube connection as the nebulizer will only accept 8 mL/min of delivery maximally at the given nebulizer setting.

TROUBLESHOOTING

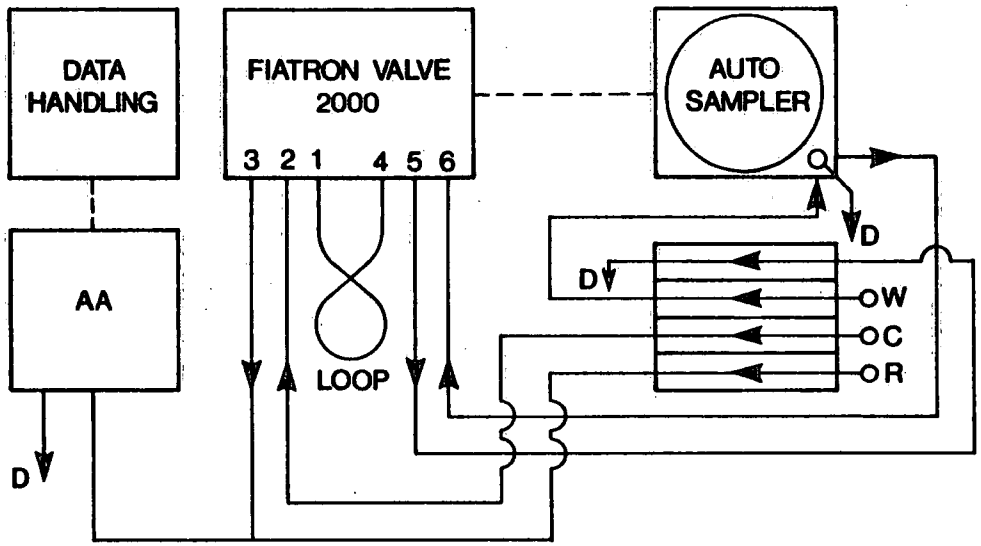
1. Bubbles in the Aspirator Line. Check to see if any of the reagent bottles are empty and check for leaks in the system. In general, bubbles in the aspirator are not usually a serious problem.
2. Leak in the Flow System. There are two types of leaks - air leaking into the system, and liquid leaking from a connection. Air leaks usually occur around the valve due to improper seal. Careful tightening of the four cap screws will fix this problem. If the leak is in a connection, re-do the connection. If the leak persists, it may be due to pressure buildup in the lines, possibly due to a clog or misalignment of the ports in the injector.
3. Erratic Performance - Poor Reproducibility. Always make sure the valve is in good working order. A partially plugged valve and/or tube assembly will cause problems. First check by unscrewing the four cap screws and pull valve apart. Check for obstructions. Also pull apart the rest of the valve assembly lines and connections and check for obstructions.
4. Sudden Decrease in Signal Height. Check the tubing system for leaks particularly in the connections (see #2 for instructions).
5. No Flow in the System. Check if the pumps are set at the proper speed. If no flow is reaching the detector, check that the pump is moving the reagent in the required direction (towards the injector and away from the reagent containers).

THE LABTRONICS DP1000 DATA HANDLING SYSTEM

To operate the LABTRONICS DP1000, consult the LABTRONICS DP 1000 Manual. For FIA operations it is esential to use the software that was designed for FIA work. The latest and current version is 3.5 which includes a "boot" disk and a "system" disk. Version 3.5 features a

variable collection rate. It should be set to 2 in the Operating Parameters. A collection rate of 2 corresponds to eight readings per second and is twice as fast as collection rate 1 and assures correct tracking of the quicker, more narrow FIA peaks.

For the calculation and reporting of results again refer to the manual. Once the raw data are in memory, the operating parameters have been entered and the layout (tray pattern) has been completed, the results can be calculated and a report with the standard curve can be quickly produced (Fig. 4).



D = DRAIN (WASTE)
W = WASH (H_2O)
C = CARRIER (H_2O)
R = 1% SOLUTION OF La

FIGURE 1. BLOCK DIAGRAM OF THE FIA-AA SYSTEM

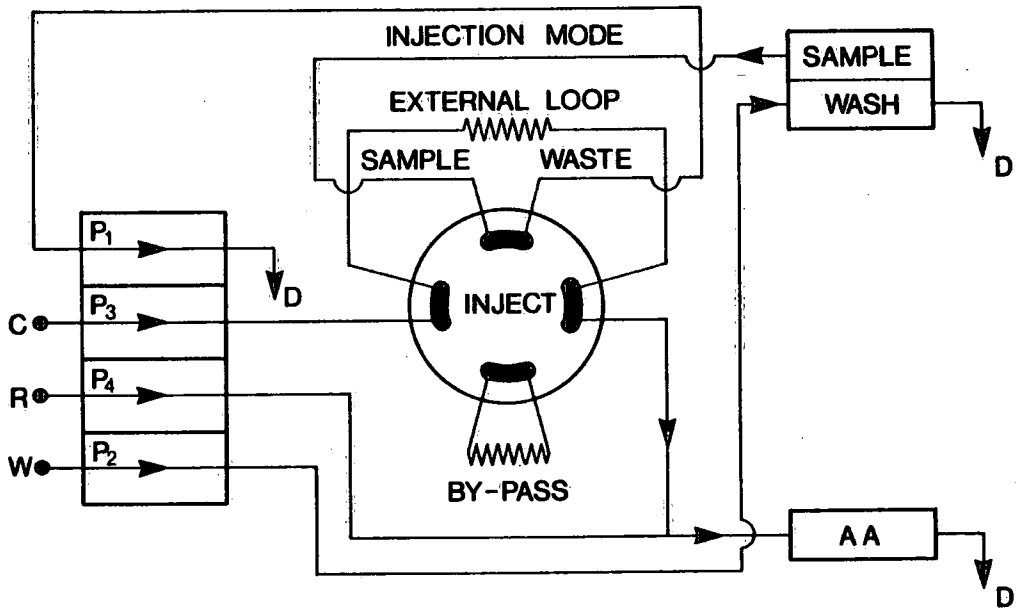


FIGURE 2. THE FIA SYSTEM INTERFACED WITH ATOMIC ABSORPTION SPECTROPHOTOMETER

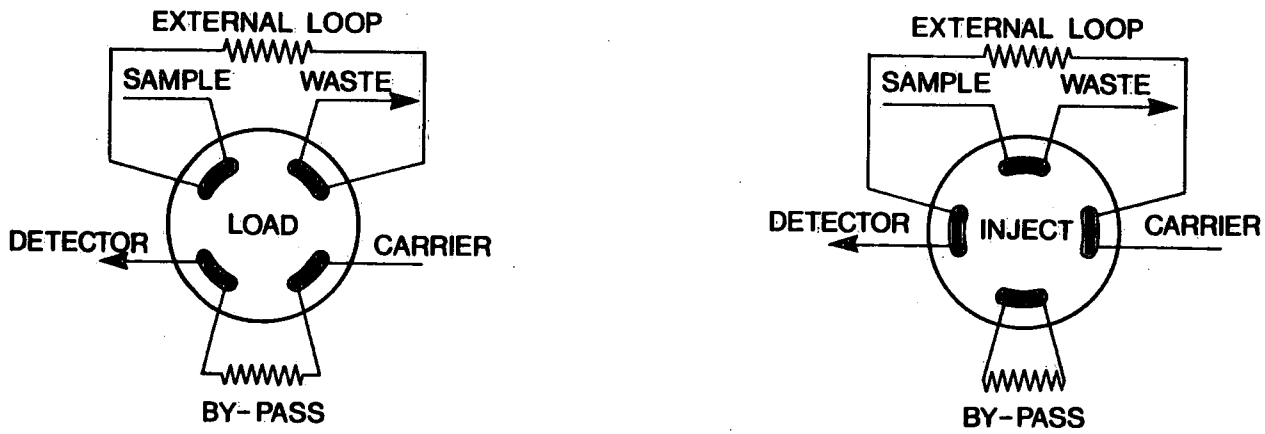
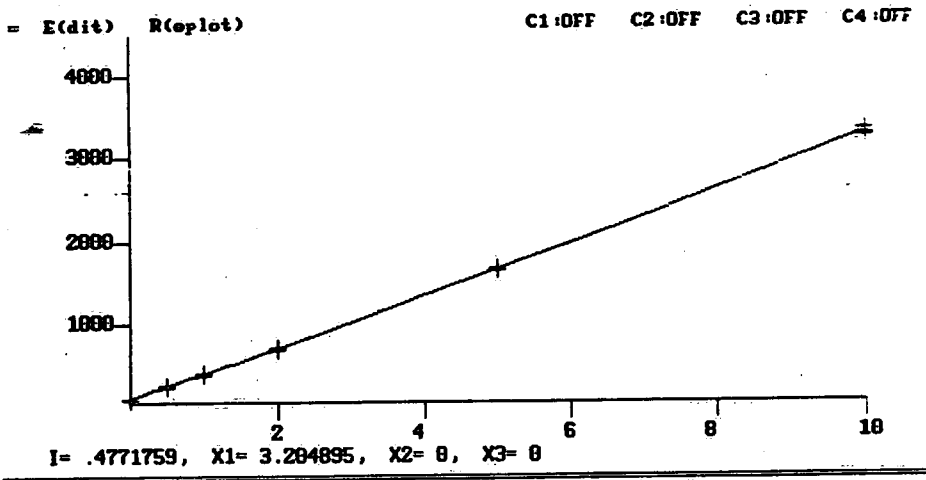


FIGURE 3. FIA VALVE IN "LOAD" AND "INJECTION" MODE



12-20-1988
RUN NUMBER: 1
OPERATOR: J.

TITLE: FIA-AA
RUN NAME: LAYOUT

LAYOUT				: FIA		
CUP#	SAMPLE ID	DIL	WGT	:PK HT	EF	MG/L :
1	S10.0	1	1	3220		9.9
2	S10	1	1	3230		9.9
3	D10	1	1	3230	D	9.9
4	S10	1	1	3304		10.2
5	S5	1	1	1635		5.0
6	S5	1	1	1660		5.0
7	S5	1	1	1650		5.0
8	S5	1	1	1660		5.0
9	S2	1	1	678		2.0
10	S2	1	1	693		2.0
11	S2	1	1	704		2.0
12	S2	1	1	689		2.0
13	S1	1	1	363		1.0
14	S1	1	1	370		1.0
15	S1	1	1	369		1.0
16	S1	1	1	368		1.0
17	S0.5	1	1	208		0.5
18	S0.5	1	1	216		0.5
19	S0.5	1	1	206		0.5
20	S0.5	1	1	204		0.5
21	SAMPLE	1	1	2539		7.8
22	DUP	1	1	2612		8.0
23	DUP	1	1	2607		8.0
24	DUP	1	1	2602		8.0
25	SPK2	1	1	3258	%	96.8
26	DUP	1	1	3269		10.1
27	DUP	1	1	3257		10.0
28	DUP	1	1	3259		10.0
29	D10	1	1	3304	D	10.2
30	DUP	1	1	3289		10.1
31	DUP	1	1	3248		10.0
32	DUP	1	1	3266		10.0
33	S0.001	1	1	39	0	-0.0
34	B	1	1	36	0	-0.0
35	B	1	1	35	0	-0.0
36	B	1	1	45	0	-0.0

FIGURE 4 A TYPICAL REPORT GENERATED BY THE LABTRONICS DP 1000 DATA ANALYSING SYSTEM