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Thermochimica Acta 243 (1994) 277–288

thermochimica acta

Controlling composition and oxidation tests of hydrocarbon and synthetic fluids in a thermal analysis laboratory ☆

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Received 28 October 1993; accepted 25 April 1994

Abstract

Statistical quality control in the thermal analysis (TA) laboratory is an integral part of good laboratory management. The rate determining step in the analysis of production samples can be customer and/or supplier/vendor input. The major task of a quality thermal analysis laboratory is satisfying the client with accurate and precise information. Control charting oxidative properties in hydrocarbon fluids is a technique to assure stability of the thermal analysis system. The composition of drain oils or the thermal stability of fluids can be ascertained by thermogravimetric methods. These procedures have been monitored with statistical process control charts. Special cause, "out-of-control" cases, will be discussed. Laboratory management can be improved by knowing the sample volume of completed thermal analysis tasks on a day-to-day or yearly basis. This information can be used to expand resources, such as automated (robotic) thermogravimetric analyzers, dual-sample differential scanning calorimeters, or additional personnel.

Keywords: Calibration; DSC; LCL; Oxidation; PDSC; Quality assurance; Statistical quality control; TA; TGA; UCL

1. Introduction

The techniques of thermogravimetry (TGA) and pressure differential scanning calorimetry (PDSC) have been used to evaluate the thermal and oxidative stability

☆ Presented at the 22nd Annual NATAS Conference, Denver, CO, 19–22 September 1993.
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SSDI 0040-6031(94)01853-9

of fluids. Compositional analyses of drain oils have also been monitored by thermogravimetry. Statistical process control tools have been applied to specific tests. Control charting is an integral tool for value management in a "production" thermal analysis laboratory [1–4]. Common and special causes have been discovered when the control sample data have been analyzed. A cause-and-effect relationship between productivity and instrument "downtime" has been observed. Sample management data have illustrated the need for additional personnel and equipment. A two-year period of data was used in this study. The use of quality management tools, e.g. histograms, flow diagrams and control charts, has improved laboratory productivity and efficiency.

2. Experimental

TGA and dual sample PDSC, TA Instruments Inc., were used in these studies. The experimental conditions used with the Model 951 TGA are given in Table 1.

The TGA system was calibrated with calcium oxalate hydrate and the melt temperatures of known materials [5].

The calorimetric studies used a dual sample PDSC, System 2000 with a 912S cell and base. The PDSC was used in the following manner: sample size 3 mg; isothermal temperature, 175°C; heating rate (to isothermal conditions), 40°C min^{-1}; atmosphere, oxygen at a flow rate of 25 cc min^{-1}, applied pressure of 500 psig; and open aluminum pans. The PDSC system was calibrated with the melting of indium and tin.

The properties measured for this TGA study were the derivative peak temperature for thermal stability of synthetic fluids (TGA(I)) and the % soot in drain oils (TGA(II)). The DSC properties measured were exothermic peak height (mW) for the oxidative stability of lubricating oils (PDSC (I)) and the oxidation induction time (OIT) (min) of hydrocarbon fluids (PDSC(II)). The control charts were established based on accepted practices of the American Society for Quality Control [6]. The X-bar average and the Upper Control Limit (UCL) and Lower Control

Table 1
Experimental conditions employed with the Model 951 TGA

	TGA(I)	TGA(II)
Temperature range in °C	25–600	25–600
Heating rate in °C min^{-1}	10	20
1st isothermal hold time in min [a]	0	20 in N_2
2nd isothermal hold time in min [a]	0	12 in O_2
Sample size in mg	5	80
Gas atmosphere	Air	N_2 and O_2
Gas flow rate in cc min^{-1}	100	50
Sample pan	Platinum	Platinum

[a] At 600°C.

Limit (LCL) were determined based on a large data set over a period of at least one year. All data points were used to establish the limits (see Figs. 2–4 and Figs. 6–9).

3. Results

The TGA(I) method reference sample is illustrated in the thermal curve in Fig. 1. Process control charts of this method for more than two years indicate both long periods of in-control temperature measurements and special cause problems accompanied with needed service (Figs. 2 and 3). Nearly all of the data are within the control limits. Some common cause variations are attributed to thermocouple replacement and cleaning of the furnace (see Figs. 2, 3 and 4). An alternative measurement was the maximum rate of the weight loss, wt% min^{-1}. A control chart of this important value paralleled the derivative peak temperature discussed above. As seen in Fig. 4, flow rate variations caused the measured property to exceed the lower control limit.

The percentage soot by the TGA(II) method is recorded in Fig. 5. Evaluation of the percentage soot from TGA(II) for 18 months indicated that one must monitor control sample composition and maintain flow control consistency, Figs. 6–9. A special cause problem was observed, resulting in out-of-control conditions, as seen in Fig. 9.

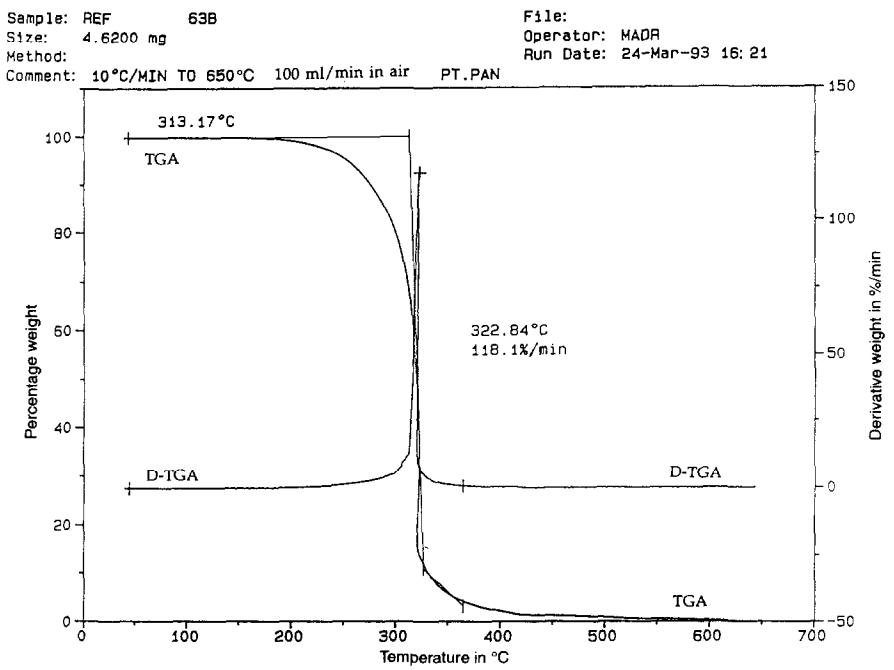


Fig. 1. TGA(I) method, reference sample.

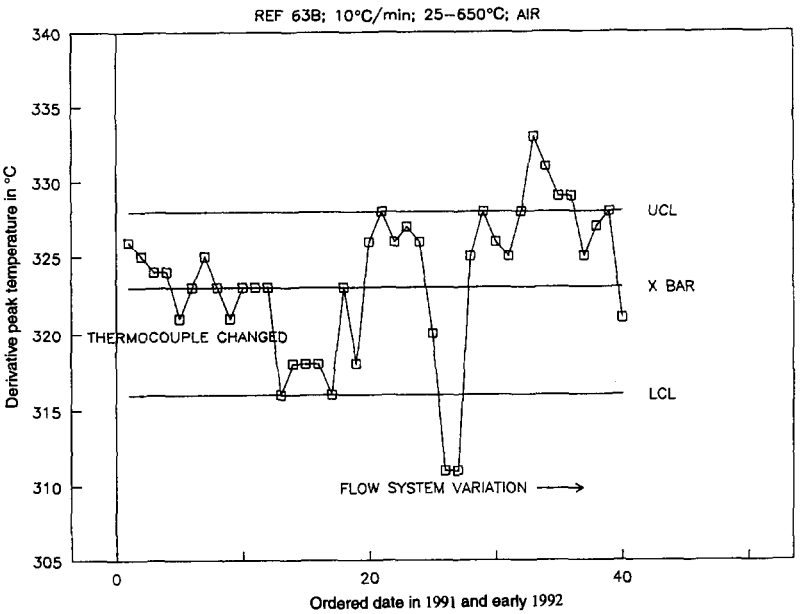


Fig. 2. TGA(I) method, individual X control chart.

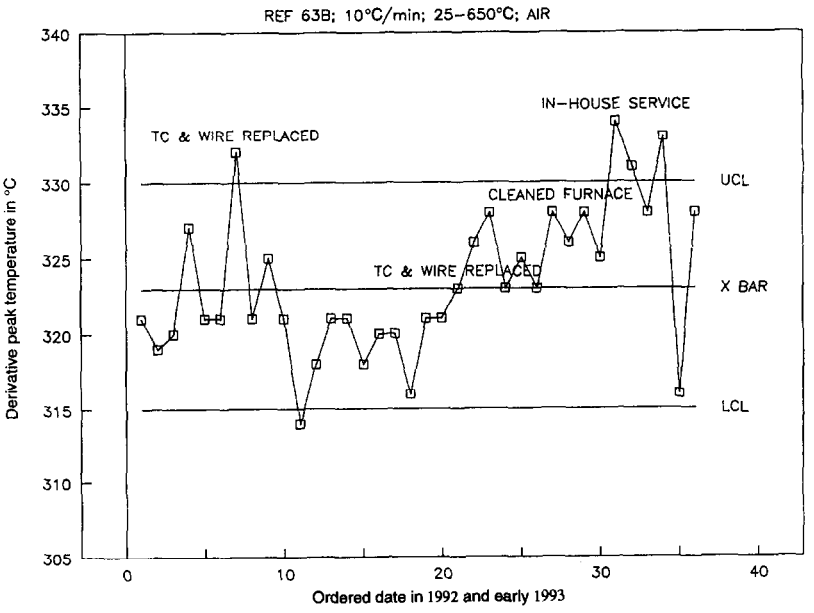


Fig. 3. TGA(I) method, individual X control chart.

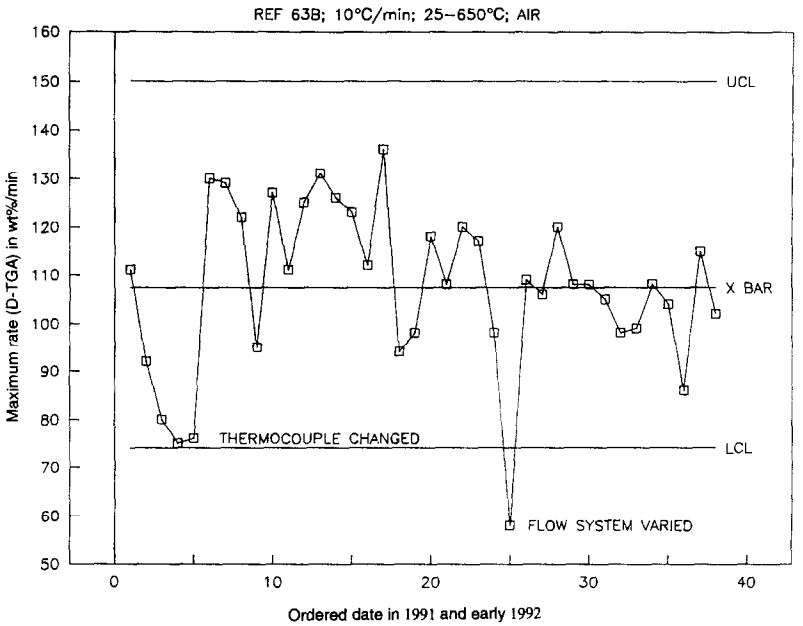


Fig. 4. TGA(I) method, individual X control chart.

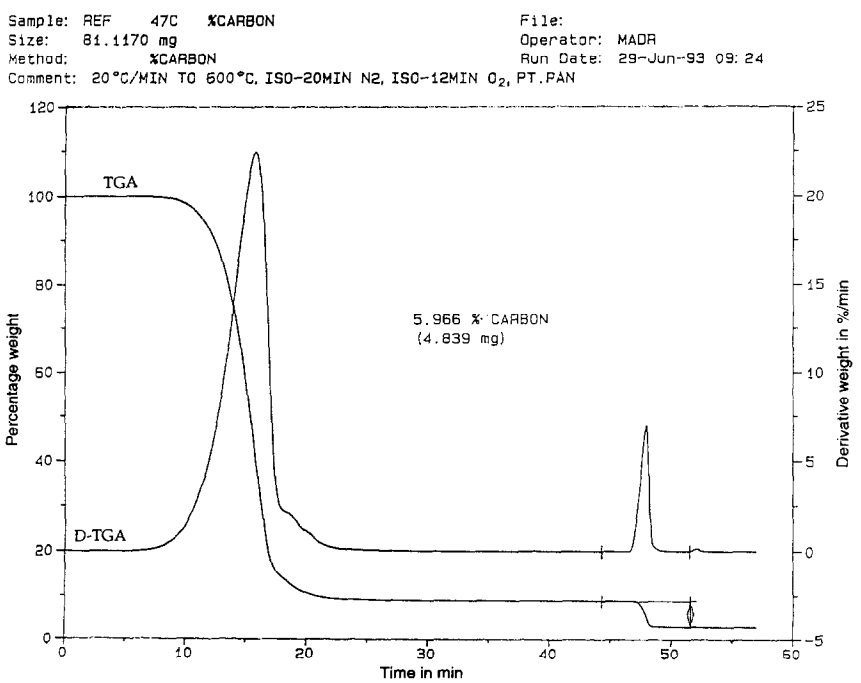


Fig. 5. TGA(II) method, percentage soot.

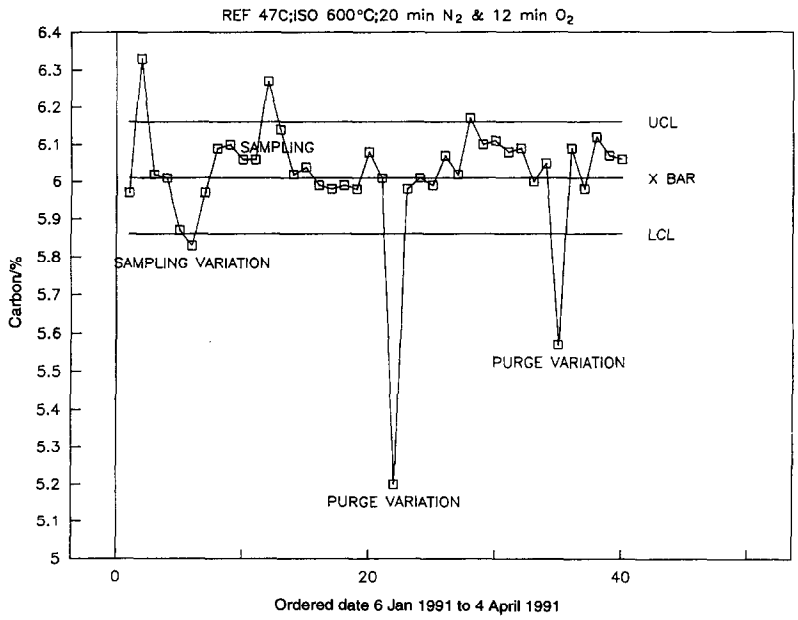


Fig. 6. TGA(II) method, individual X control chart.

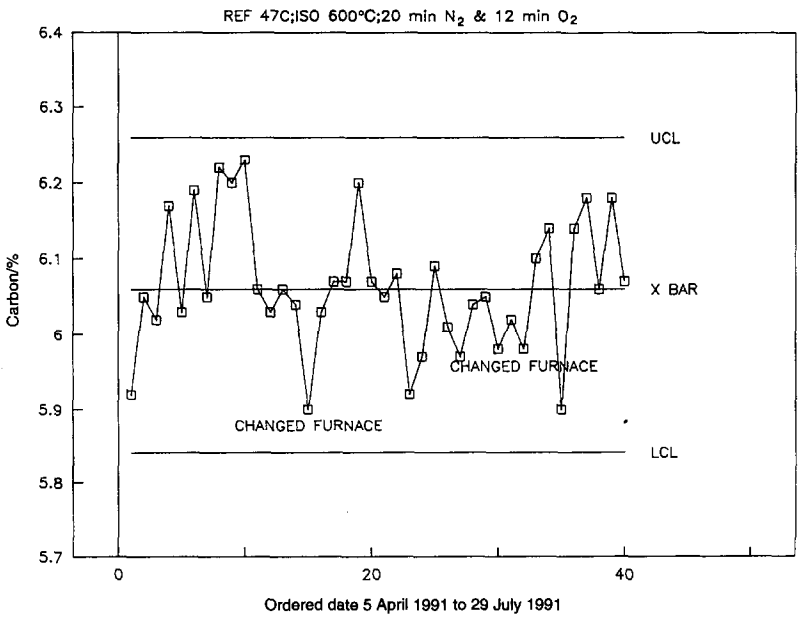


Fig. 7. TGA(II) method, individual X control chart.

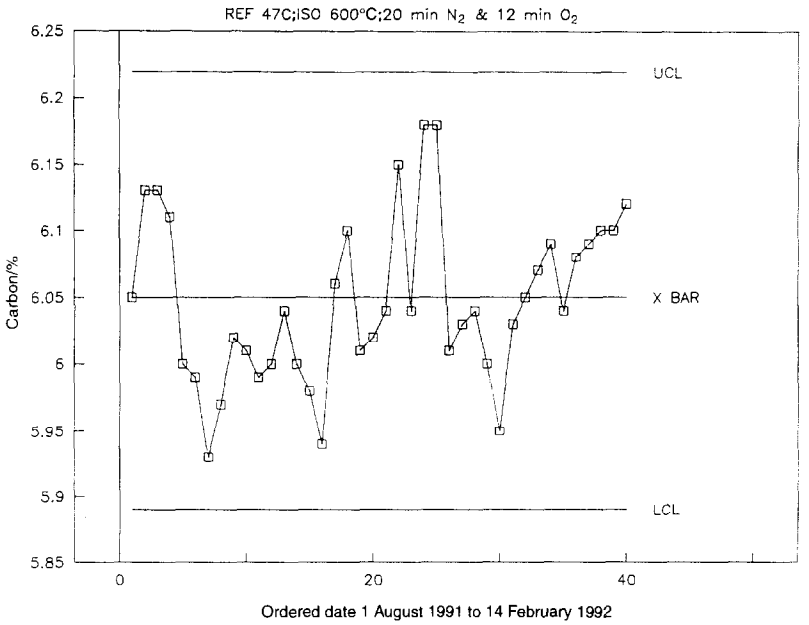


Fig. 8. TGA(II) method, individual X control chart.

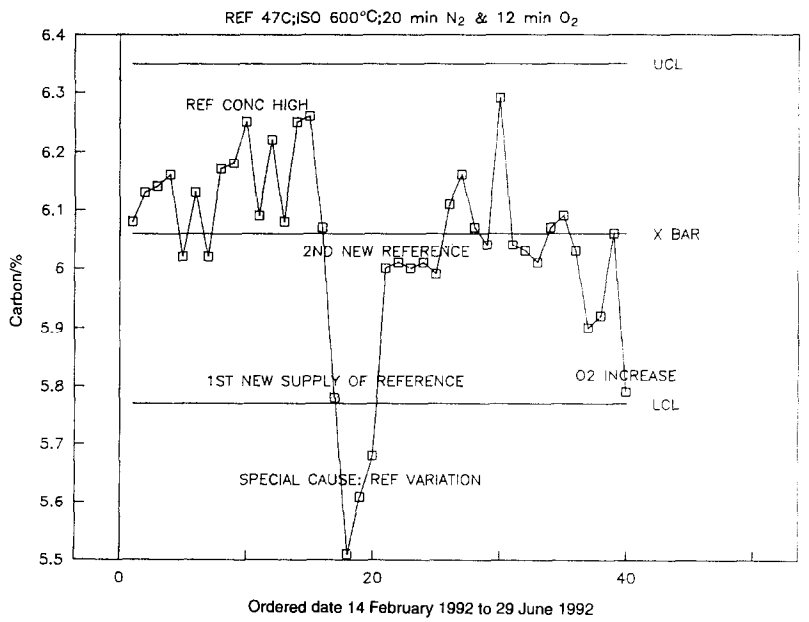


Fig. 9. TGA(II) method, individual X control chart.

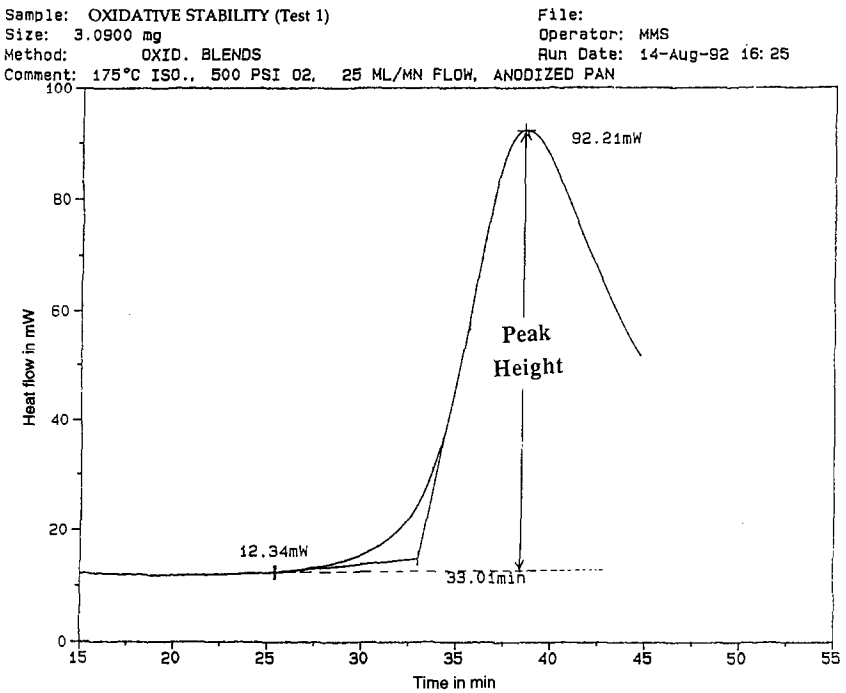
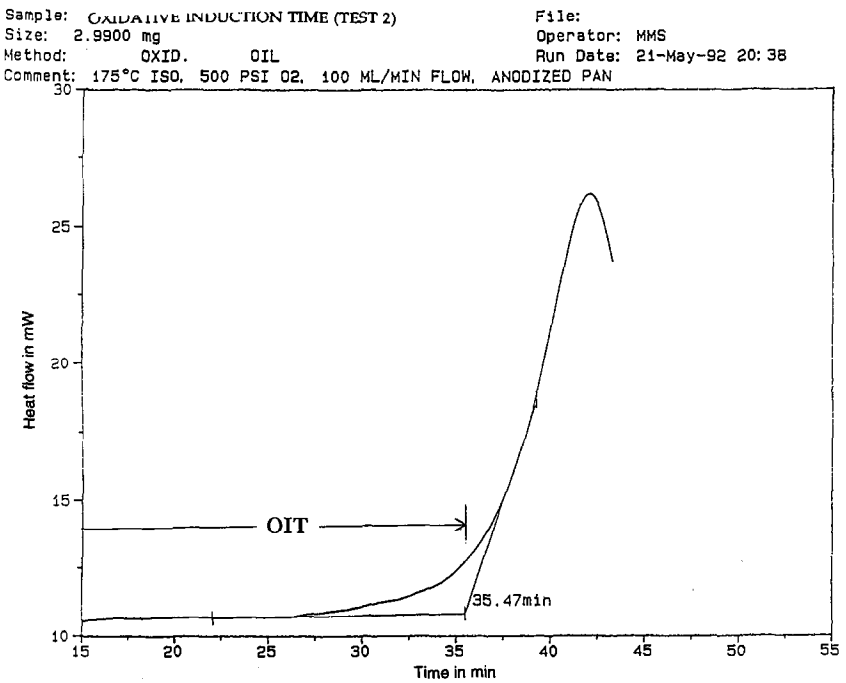
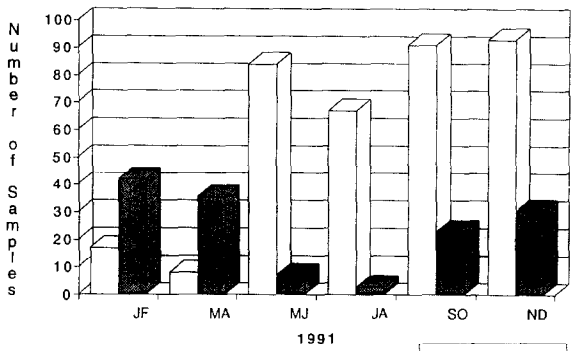


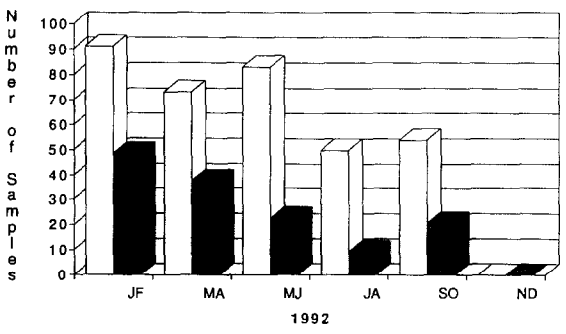
Fig. 10. Oxidative stability by PDSC(I); peak height of an oxidation process.





JF = January/February
MA = March/April
MJ = May/June
JA = July/August
SO = September/October
ND = November/December

Fig. 12. PDSC(I), bi-monthly response time.



JF = January/February
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JA = July/August
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Fig. 13. PDSC(II), bi-monthly response time.

The largest volume of test samples is for oxidative stability by PDSC. For example, Fig. 10 depicts a peak height of an oxidation process and Fig. 11 the oxidation induction time (OIT) of a blend.

Typically, a large number of lubricating oil samples are evaluated by PDSC over a two-shift period on a day-to-day basis. Therefore, the time of response for this large batch of samples is critical to our customers, both external and internal.

Fig. 11. Oxidative stability by PDSC(II); oxidative induction time.

Figs. 12 and 13 (PDSC (I) and (II)) illustrate that test response time (days) were best (lowest) during the months of May through August. Summer interns, college students, fill the gap for analyzing the large batch of Lubrizol and ASTM research samples that accumulate with time. Additional laboratory fulltime second-shift assistance lowered the turn-around time during the months of May through August by 80–90%. Acquisition of additional dual sample PDSCs between 1991 and 1992 also improved the response time. The combination of equipment failure, large volumes of other test requests and new operator training, produced large response times.

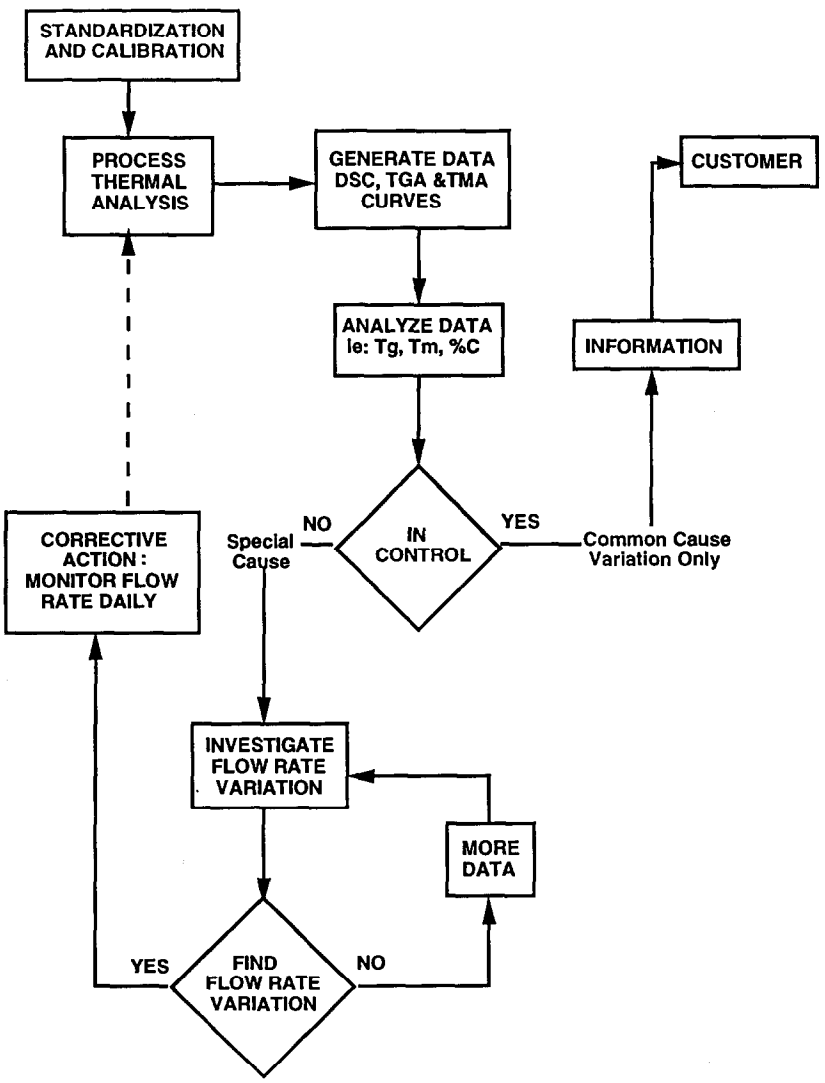

Fig. 14. Thermal analysis process flow chart: statistical quality control.

A study of the thermal analysis process, using a flow chart, aids the analyst by more easily directing the analyst through the critical paths of TA tests. Figure 14 is a scheme for statistical quality control of a TA test. Illustrated in this figure are the decision processes when a special or common cause problem is observed in a control chart. The properties measured, e.g. T_g, melt temperature or percentage soot, can go out-of-control and an investigation of the variables is necessary. The example cites a flow rate variation, observed in Figs. 2, 4 and 6. Corrective action is accomplished by monitoring the flow rate daily and making appropriate instrumental adjustments. A flow diagram can also be used to instruct the technical staff on infrequently used ASTM or in-laboratory tests. This format can clearly point out safety features and required maintenance.

Instrument downtime is detrimental to the operation of a thermal analytical laboratory. An evaluation was made of the number of service calls in 1991 and 1992 versus number of production samples run in the thermal tests described above. In 1991 there was an apparent correlation between the number of samples and service calls, see Fig. 15. The number of samples increased to approximately 100 per month and the service calls increased from one to four in the same time period. During this period, training and development of operators was also occuring. For the last two months of 1991 and all of 1992 there was no correlation between service and productivity (Fig. 16). As the capacity of the laboratory for tests was reached, the total number of samples that could be tested and maintained by highly skilled operators was attained. Once maximum level was achieved, production was apparently not a factor of downtime, because established protocols were written and finalized and operator training was fully completed.

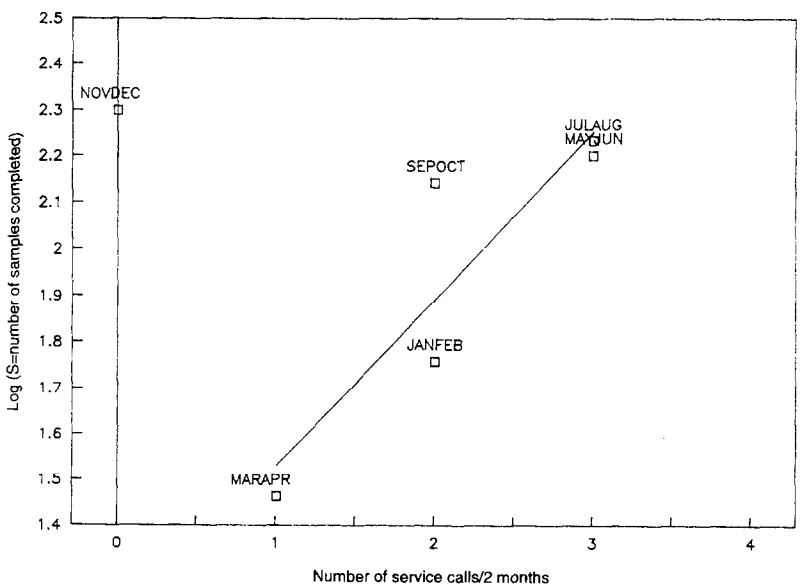

Fig. 15. Laboratory management evaluation: number of production samples vs. service in 1991.

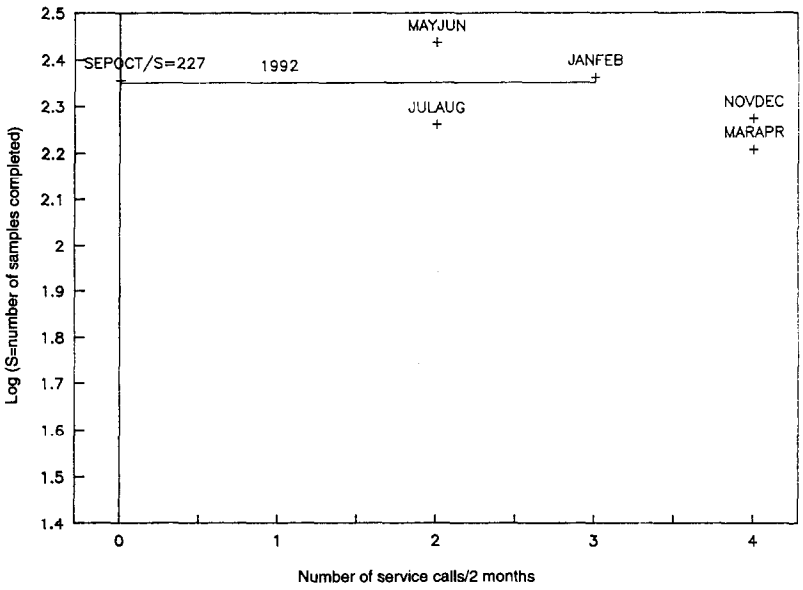

Fig. 16. Laboratory management evaluation: number of production samples vs. service in 1992.

4. Conclusions

TGA method I, illustrates that replacement of thermocouples and cleaning/repairing of the furnace are common cause variations. However, flow rate problems, as demonstrated in TGA method II, constitute a special cause problem. Pressure differential scanning calorimetry data showed that the mid-year months had the "best service" (lowest response times) which coincided with the utilization of additional personnel, i.e. summer interns. Enhanced response time was also noted when two samples were analyzed at a time, when utilizing the dual sample PDSC. A thermal analysis flow diagram was useful in training lab personnel in collecting valued information for customers.

References

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