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DEDICATED, AUTOMATIC GAS CHROMATOGRAPH FOR MONITORING SULPHUR GASES

T. L. C. DE SOUZA

Environmental Control Section, Pulp and Paper Research Institute of Canada (PAPRICAN), 570 St. John's Boulevard, Pointe Claire, Québec H9R 3JG (Canada)

SUMMARY

The development of an automatic gas chromatograph dedicated to the analysis of sulphur compounds from flue gases is described. It uses a special gas-separating column with a sulphur-specific flame-photometric detector. A microcomputer controls all valve functions (sample and calibration gas injections), temperature and pressure settings, data gathering and processing, numerical calculations of concentrations and report print-out. Analysis of compounds such as hydrogen sulphide, carbonyl sulphide, sulphur dioxide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide in concentrations of up to 100 ppm is accomplished in repeat cycles of about 10 min. Higher concentration ranges can be measured by reducing the sample volume.

INTRODUCTION

Sulphur gases of unpleasant odour are produced in the kraft process of making pulp for paper manufacture. Principally, they comprise hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide, together referred to as total reduced sulphur (TRS) compounds. Sulphur dioxide and odourless carbonyl sulphide are also produced, the latter usually when the chemical recovery furnace in the kraft process is overloaded.

In early 1970, the two most frequently used monitors for the analysis of sulphur dioxide and TRS compounds were the Barton coulometric titrator and the Du Pont Model 460 UV sulphur dioxide-TRS analyzer. In both these instruments, TRS compounds are oxidized to sulphur dioxide prior to actual measurements, although this step can be avoided in the first analyzer. Limitations of the coulometric analyzers when used in either one of two modes (with/without oxidation) have been described in detail elsewhere¹. The step of oxidizing TRS compounds to sulphur dioxide inadvertently includes other non-regulated compounds, like carbonyl sulphide, thus giving unduly high "TRS" readings. These incorrect measurements are known to cause pulp mills to cut back production in order to comply with existing TRS emission limits.

Although it was generally known that the most reliable way of measuring

concentrations of sulphur gases was by gas chromatography (GC), the procedure, when used with grab-sampling, offered only periodic analyses. Regulations stipulated continuous or high-frequency monitoring of TRS, hence, the need to automate the GC instrumental technique. Earlier, we had developed a GC column (later known as Supelpak-S^{2,3} capable of separating carbonyl sulphide, sulphur dioxide, and all four TRS compounds of regulatory interest. The column was unaffected by water vapour (*ca.* 30%) found in furnace flue gases. Another infant technology of the time was the development of microprocessors that enabled automatic control of various instrument functions, collection and processing of data, and calculation and printing of the concentrations of the compounds analyzed. These two important developments enabled us to build an automatic, reliable, accurate and a dedicated TRS-monitoring GC⁴. Later, this technology was transferred to Western Research & Development (Calgary, Alberta, Canada) that now manufactures it under license. The commercial units, Model 800 TRS analyzers, have been used to study performances of TRS-control scrubbers and to monitor TRS for compliance purpose. Many automatic GC procedures⁵⁻¹³ were described in literature in order to monitor air pollutants, but few¹² were dedicated to the monitoring of TRS.

EXPERIMENTAL AND RESULTS

Laboratory prototype monitor

Equipment. The gas sampling probe was a 1.27 cm I.D. stainless-steel tube, with a plug (2–5 cm) of fine glass wool at the tip of the tube for retaining most of the particulates from the sample flue gas (Fig. 1). Sampling line was *ca.* 30 m × 0.4 cm I.D. Teflon (PTFE) tubing, which is inert to sulphur gases. Sample loops (0.5–2.5 ml), packed separating column tubings, and all connecting lines were also made of PTFE. Prime mover was a peristaltic pump (Masterflex) with a single head and variable-speed drive, purchased from Cole-Parmer Instrument, (Chicago, IL, U.S.A.). Flexible tubing in the pump head was of silicone rubber. Separating columns were three short, packed columns. They were made of 2 mm I.D. PTFE tubing and consisted of (i) a "stripper" column, (ii) separating column 1 and (iii) separating column

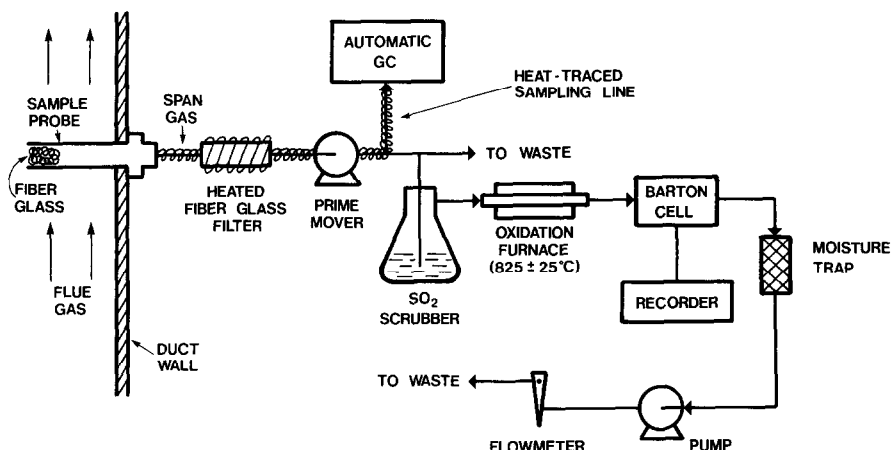


Fig. 1. Typical gas sampling train used in sulphur gas analysis.

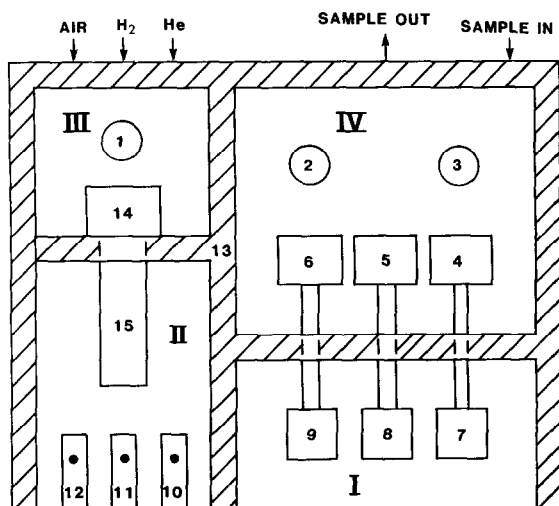


Fig. 2. Schematic diagram of the arrangement of the major components in the GC unit. Sections I and II at ambient temperature, Section III at 130°C and 1 = Supelpak-S column, 2 = column 1 of Parapak Q, 3 = Stripper column of Porapak Q, 4 = stripper valve, 4-port, 5 = sampling/calib. valve, 4-port, 6 = sampling valve, 10-port, 7-9 = valve actuators, 10-12 = flow-rators for He, H₂, air, 13 = insulated wall of sections, 14 = burner of FPD, 15 = photomultiplier tube.

2, with lengths of 1.3, 67.0 and 16.5 cm, respectively. The first two columns were packed with acid-washed Porapak Q and maintained isothermally at 78°C. Column 2 was packed with specially treated Porapak QS (Supelpak-S) and maintained at 130°C.

The microcomputer, TRS display unit and permeation oven were built and programmed at PAPRICAN. Valco 10- and 4-port valves were of Carpenter stainless-steel from Chromatographic Specialties (Brockville, Canada). Valve actuators were from Technical Marketing Assoc. (Pointe Claire, Canada). The flame photometric detector was a single-flame detector with a 394-nm filter, purchased from Tracor (Austin, TX, U.S.A.). Strip-chart recorder was a Honeywell Elektronik-19 from Honeywell (Philadelphia, PA, U.S.A.). Printer was a Teletype Model RO-33 from Teletype (Skokie, IL, U.S.A.).

GC construction. The GC apparatus was an insulated metal box, divided into four sections (I-IV), as shown on Fig. 2. Section I held the sample valve actuators, while section II contained gas flow-rators, permeation tubes, and the photomultiplier tube of the flame photometric detector. Both sections were maintained at room temperature (*ca.* 25°C). Section III contained the main column (Supelpak-S) and the flame photometric detector, while section IV held the Valco valves and two gas-separating columns. These sections were maintained at 130°C and 78°C, respectively.

Design of the monitor. The prime mover, placed downstream of the fine particulate filter (Fig. 1), directed a synthetic mixture of gases mentioned in the Introduction or real flue gases (1-2 l/min) through the sample probe and heated (105 ± 5°C) sample line to waste. A portion of the above gas flow (100-200 ml/min) was drawn into the sample loop of the gas chromatograph by means of an air-operated aspirator.

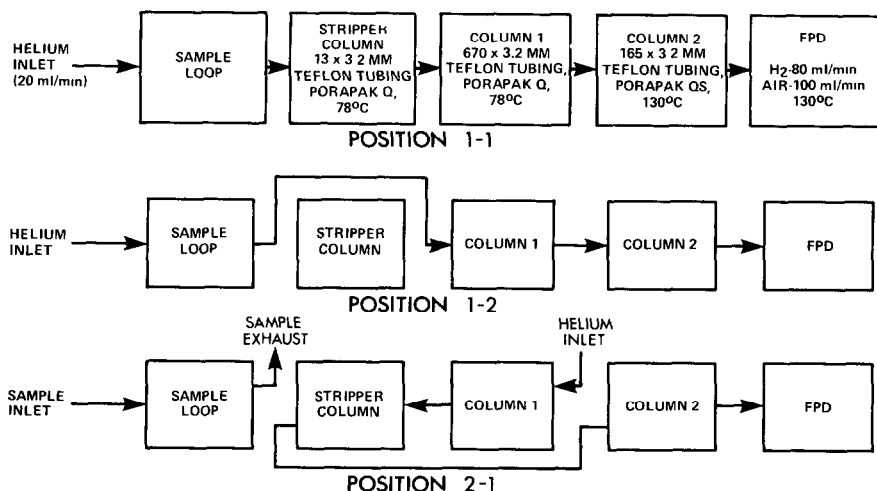


Fig. 3. Schematic diagram of the dual valve separation procedure. FPD = flame photometric detector.

A custom-programmed microcomputer data acquisition (MCDA) system controlled the sampling and injecting sequence of the sampling valve. The injected mixture of gases was separated by the column configuration into individual components prior to being directed to the flame photometric detector (Fig. 3). Two 4-way valves and a 10-port valve were sequenced in such a way as to trap and then release (by back-flushing) the heavier sample gas components⁴. Lighter components passed rather rapidly through the separating columns and on to the flame photometric detector, followed by the backflushed heavier gases. In position 1-1, the sample was swept out of the sample loop into the stripper column which retained the higher molecular-weight compounds, *viz.*, dimethyl sulphide and dimethyl disulphide, while allowing the lighter ones, *viz.*, hydrogen sulphide, carbonyl sulphide, sulphur dioxide and methyl mercaptan, to pass through. The stripper column was then isolated from the system (position 1-2), thereby preventing further movement of dimethyl sulphide and dimethyl disulphide. Once the separation of the lower-molecular-weight compounds was achieved, the system was switched to position 2-1. In this position, dimethyl sulphide and dimethyl disulphide were backflushed from the stripper column into column 2, where they were effectively separated and led to the flame photometric detector.

The GC conditions used were: sample volume, 0.5–2.5 ml; detector temperature, 130°C; carrier gas (helium), 20 ml/min; hydrogen, 80 ml/min; air, 100 ml/min; stripper and column 1 temperature, 78°C; column 2 temperature, 130°C.

The signal from the detector was monitored with the stripchart recorder. The areas of chromatographic peaks, obtained in terms of analog signals, were converted to digital readings. Using calibration data stored in the memory of the MCDA, the digital readings were converted to concentrations (ppm) of each individual gas, and TRS values were calculated and printed. An option to display the concentration of the latest TRS analysis at a distance of up to 75 m from the analyzer, *e.g.* in the control room of the chemical recovery furnace, was available. This would allow the operator to take corrective actions if needed.

TABLE I
ANALYSIS PRINTOUT OF A TYPICAL 6-COMPONENT GAS MIXTURE

Gas	Start*	Max*	End*	Area	ppm
H ₂ S	00048	00055	00066	15 414	0009.1
COS	00066	00074	00115	09299	0001.2
SO ₂	00115	00133	00230	22 549	0016.8
RSH**	00230	00270	00297	42 926	0010.6
R ₂ S	00397	00428	00481	11 053	0002.1
R ₂ S ₂	00481	00536	00720	06423	0000.7
TRS					0023.2

* Entries are times, in seconds, from time of injection.

** R = CH₃

Performance of the GC monitor. Calibration curves were generated with mixtures of standard sulphur gases. Each of the six sulphur gases had a different curvilinear relationship for a 2.5 ml sample volume and concentration range of 1–100 ppm. The fitting of the multi-point calibration curves became more complex than two point curves, since the fits took the form of polynomial equations. To handle these equations, a floating-point number system was added to the GC monitor software program. The calibration curves were fitted on the Institute's mainframe computer, using a regression routine. The results from that program were then transferred to the memory of the GC microcomputer. Calibration checks were performed at mill site on a regular basis. The identity of individual components was established, using retention-time "windows". An example of the final printout of this laboratory prototype GC can be seen in Table I.

The chromatographic columns used in the monitor logged *ca.* 4000 h out of which *ca.* 1200 h included exposure to "real" kraft recovery furnace flue gases. Insignificant changes in retention times of specific sulphur compounds were noted, which indicated minimal deterioration of the columns. Calibration curves showed \leq 10% change during the whole testing period. The overall system proved to be rugged, and exposure to the kraft mill environment for *ca.* 1500 h did not cause corrosion or other failures of component parts of the GC or the microcomputer.

Results of analysing the same flue gases with the GC monitor, Barton titrator, and a Du Pont Model 460 sulphur dioxide-TRS analyzer verified earlier assumptions of positive errors obtained with the last two instruments (Fig. 4). This finding established that of the three continuous monitors tested, the dedicated automatic GC monitor was the most accurate.

Commercial Model 800 TRS analyzer

Equipment. The analyzer consists of three component parts *viz.* a sample conditioning unit (SCU) normally mounted on flue gas ducts or stacks, a heated ($100 \pm 2^\circ\text{C}$) sample line (30 m \times 0.4 cm I.D. PTFE tubing) and the analyzer with all electronics. The latter is housed in a walk-in, weatherproof, temperature-controlled shelter approximately 1.8 \times 1.8 \times 2 m. Sample conditioning unit consists of a stainless-steel probe, sample valves and electronics. The unit is operated at 120°C.

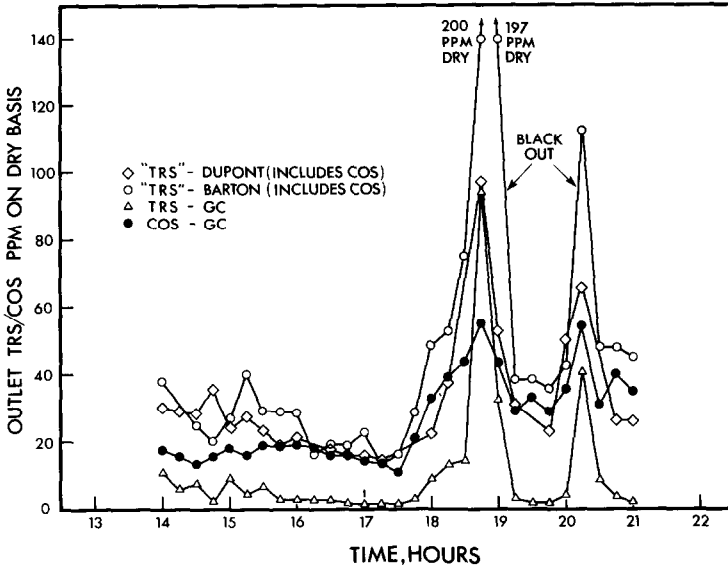


Fig. 4. Simultaneous analyses of three TRS monitoring instruments at a pulp mill. The high TRS-carbonyl sulphide emissions shown as "Black-outs" correspond to temporary loss of flame in the recovery furnace.

Sampling line consists of two PTFE tubes (0.2 and 0.4 cm I.D.) running side by side (Fig. 5) used to transport calibration and sample gases, respectively. They are multi-covered in a cable for insulation and protection and its temperature controlled at $100 \pm 2^\circ\text{C}$. The GC oven consists of two aluminium plates approximately $13 \times 13 \times 1.3$ cm with just enough room in between them to house a separating column. The design of the oven is kept simple and small in order to facilitate rapid heating by a high-output air heater. Cooling of the oven in 1.0–1.5 min is obtained by means of a Vortex tube (Vortec Corporation, Cincinnati, OH, U.S.A.) operated with instrument air at 689 kPa. The flame photometric detector is a dual-flame detector (Varian Canada, Georgetown, Ontario, Canada) whose response to sulphur compounds is independent of their molecular forms.

Design of the analyzer. The flow of gases to the GC oven is shown on Fig. 6. Sample or calibration gas is drawn into the sample loop with an air aspirator. A

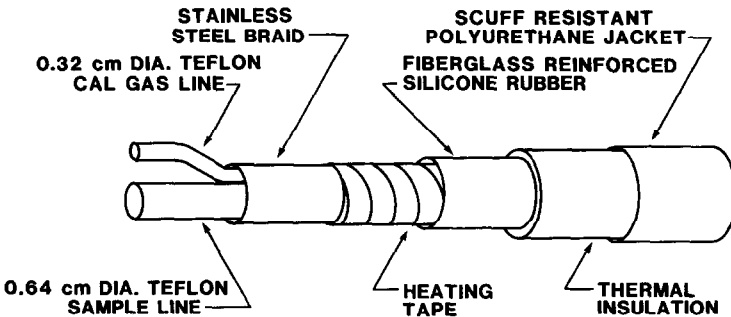


Fig. 5. A cut-away view of the sample line.

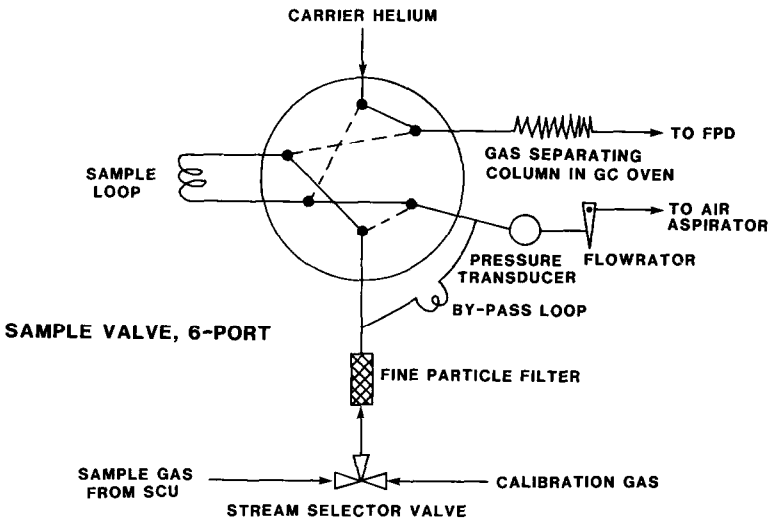


Fig. 6. Schematic diagram showing gas flows within the main oven.

pressure transducer and a rotameter are used to regulate gas flow-rate. Most of the gas flow is diverted around the injection valve through a bypass. Helium is used to carry the sample gas from the loop (typically 0.5 ml) to the flame photometric detector via the single separating column, similar to Supelpak-S^{2,3}. Particle buildup in the probe is prevented by back-flushing with air (Fig. 7). The design of the GC oven allows rapid cooling and hence the use of a single column with temperature programming.

Typical GC conditions used are: Separating column, proprietary; sample volume, 0.5 ml; inject. port temperature, 100°C; detector temperature, 100°C; air 1, 80 ml/min; air 2, 170 ml/min; hydrogen gas, 140 ml/min; carrier gas (helium), 30 ml/min; and temperature program, 60°C (1 min), then raised at a rate of 30°C/min to 200°C (2 min).

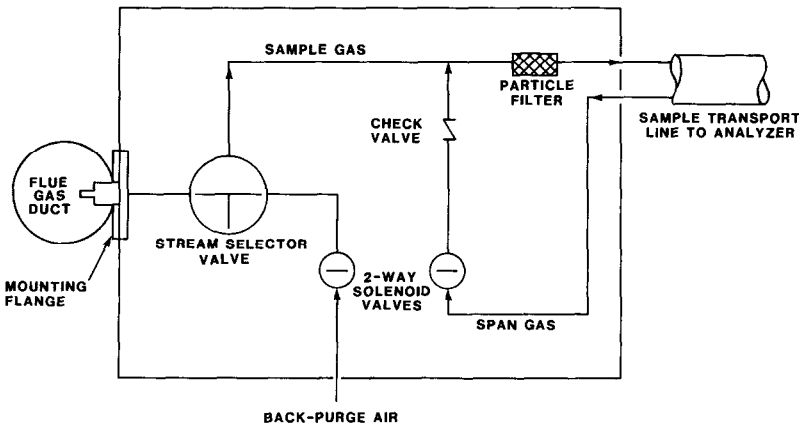


Fig. 7. Schematic diagram of the sample conditioning unit.

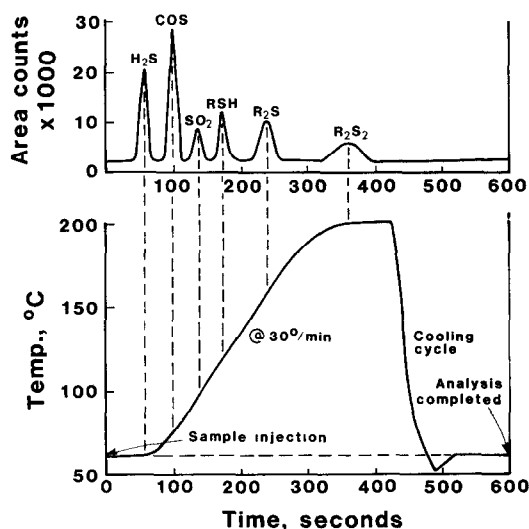


Fig. 8. Typical gas chromatogram obtained with the Model 800 TRS monitor. R = CH₃.

A temperature program profile and a typical chromatogram obtained are shown on Fig. 8. It can be seen that total analysis time is less than 10 min with good resolution of the six sulphur gases analyzed.

Calibration. The need to calibrate with all standard sulphur gases was overcome by the use of a dual-flame Varian flame photometric detector which oxidizes sulphur gases to sulphur dioxide in the first flame. The second flame, which rests

TABLE II

REPORT FORMAT OF THE MODEL 800 TRS ANALYSER

Gas concentrations in ppm.

81/11/01	Time	P	T	#?	H ₂ S	COS	SO ₂	RSH*	R ₂ S	R ₂ S ₂	TRS
PRECIP O/L	16:00	646	374	01	28	34		4.7		0.8	34
AUTO CAL CHANGE** = 1.1%											
GC CAL GAS	16:13	611	374		4.7	25					4.7
PRECIP O/L***	16:25	643	373		24	29		3.1	0.8		2.8
PRECIP O/L	16:36	646	371		30	33		5.0			35
PRECIP O/L	16:47	645	372		42	32		3.5	1.5		47
PRECIP O/L	16:57	646	372	01	22	36		4.6			27
PRECIP O/L	17:08	645	372	01	26	40		4.1			31
PRECIP O/L	17:19	648	371	01	21	32		3.7			25
PRECIP O/L	17:29	647	371		20	27		2.8		1.2	25
PRECIP O/L	17:44	649	374	01	34	34		4.5		1.0	41
PRECIP O/L	17:54	648	371	01	30	32		5.1		0.9	37
PRECIP O/L	20:05	647	372	01	30	36	2.3	3.7		1.4	37
PRECIP O/L	20:15	649	372	02	26	32		4.3		1.3	33

* R = CH₃.

** Automatic calibration change.

*** Precipitator outlet.

directly above the first, excites the formed sulphur dioxide gas which then emits light that is measured with the detector. This way, only one sulphur gas need be used for calibration purposes in order to compute concentrations of all other sulphur gases.

The most stable and least polar of the TRS gases, *viz.* carbonyl sulphide, was chosen as the calibration gas. It is injected before the fine particulate filter in the SCU to check for leaks in the sample train and for TRS losses (if any) from the SCU to the detector (Fig. 7). Routinely, it is injected closer to the detector, *viz.* before the 6-port sampling valve. Calibration is performed and the data computed automatically once in every 8 h or as desired.

Although direct detector response is the same for all six sulphur compounds, the recovery of each of them after passing through the separating column is not the same. Hence, use is made of relative response factors (relative to carbonyl sulphide) which are incorporated into the analyzer software.

The final report printout (Table II) includes the following information: date, time of analysis, automatic calibration change if any, sample identity *e.g.* precipitator outlet, sample pressure (P, in mmHg), sample temperature (T in K), number of unidentified peaks (#?), if any, concentration of each gas (in ppmv), concentration of TRS as hydrogen sulphide and a running 24-h average TRS value.

CONCLUSION

The model 800 TRS analyzer has some safety aspects that automatically shut off hydrogen in the event of detector flame-out. Failure of critical components, automatically shuts down the system and relays an appropriate message to the operator. The system has a built-in security code that prevents unauthorized personnel from tampering with the software. Also, an alarm is raised if set TRS guideline concentrations are exceeded.

Downtime of the monitor in its first year of operation at a mill in Canada was only 5%. An audit of the monitor carried out by a government agency indicated no deviation from the baseline when "zero" air was analyzed. Calibration error over the range of 0 to 100 ppm of hydrogen sulphide from a permeation tube was reported to be less than 5%. As much as 35 ppm of carbonyl sulphide was analyzed with the monitor from the emissions of their overloaded recovery furnace. Without the monitor, the carbonyl sulphide could have been included in the TRS figure making it appear to have exceeded the limit of 26 ppm of TRS, when in fact it did not.

REFERENCES

- 1 T. L. C. de Souza, D. C. Lane and S. P. Bhatia, *Pulp Paper Can.*, 76 (1975) 73.
- 2 T. L. C. de Souza, D. C. Lane and S. P. Bhatia, *Anal. Chem.*, 47 (1975) 543.
- 3 T. L. C. de Souza, *J. Chromatogr. Sci.*, 22 (1984) 470.
- 4 T. L. C. de Souza, R. Wostradowski, R. Poole, O. Vadas, S. P. Bhatia and S. Prahacs, *Pulp Paper Can.*, 79 (1978) T242.
- 5 T. E. Applebury and M. J. Schaer, *J. Air Pollut. Control Assoc.*, 20 (1970) 83.
- 6 R. K. Stevens and A. E. O'Keefe, *Anal. Chem.*, 42 (1970) 143A.
- 7 R. L. Chapman, *Environ. Sci. Technol.*, 8 (1974) 520.
- 8 F. Baumann, A. C. Brown III, S. P. Cram, C. H. Hartmann and J. L. Hendrickson, *J. Chromatogr. Sci.*, 14 (1976) 177.
- 9 E. M. Emery, *J. Chromatogr. Sci.*, 14 (1976) 261.

- 10 C. V. Philip, J. A. Bullin and R. G. Anthony, *J. Chromatogr. Sci.*, 17 (1979) 523.
- 11 H. L. Gearhart, R. L. Cook and R. W. Whitney, *Anal. Chem.*, 52 (1980) 2223.
- 12 J. C. Laird, J. E. Nelsen and R. L. Tomlin, presented at the *72nd Annual Meeting of Air Pollut. Control Assoc., Cincinnati, OH, 1979*, paper No. 79-6.4 APCA, Pittsburgh, 1979.
- 13 L. Huber and H. Obbens, *J. Chromatogr. Sci.*, 349 (1985) 465.