CSIRO

INSTITUTE OF ENERGY AND EARTH RESOURCES

DIVISION OF FOSSIL FUELS

SULPHIDE EMISSIONS FROM CATALYST-EQUIPPED CARS
IN AUSTRALIA

REPORT TO THE DEPARTMENT OF THE ARTS, SPORT, THE
ENVIRONMENT, TOURISM AND TERRITORIES

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SUMMARY

The emission of reduced sulphur compounds from catalyst-equipped vehicles has been studied using an on-line real time sulphur analysis system. Such emissions occur when reducing conditions exist in the catalyst and are associated with periods of heavy acceleration or braking. For significant levels of odorous sulphur compounds to be emitted, the catalyst temperature needs to be greater than 300°C. The emissions increase with increasing fuel sulphur content. It is concluded that, as it is difficult to avoid rich excursions (i.e. reducing conditions in the exhaust gas), reduction of the sulphur content of fuel is the only feasible method of control.

1. INTRODUCTION

Sales of catalyst-equipped cars in Australia began in August 1985, soon after the introduction of unleaded petrol (ULP). In April, 1986, complaints about unpleasant odours from the new cars emerged. These received wide coverage in the press and on television, partly because many of the complaints originated in Canberra, particularly from the Federal Government's ministerial drivers. Nevertheless, the phenomenon appears to be widespread, although of fairly low incidence. A request over Sydney radio by the NRMA for information about individual vehicles with an odour problem elicited about 200 calls within 2 hours with a total of about 600 to date.

It was apparent that three factors were involved in the emission of odours : the presence of a catalytic converter (catalyst), sulphur (S) in the petrol and reducing conditions in the exhaust.

The State Pollution Control Commission of New South Wales (SPCC), after a review of the literature, initiated an investigation carried out by the University of NSW of the chemistry occurring in the catalyst (Trimm, 1986). The study confirmed that fuel sulphur and the presence of reducing conditions in the exhaust gas were the primary causes of odours. It was recommended that the relationship between fuel sulphur levels and sulphide emissions be further explored.

In parallel with the study of Trimm (1986), the SPCC carried out tests on private complaint vehicles. The procedure consisted of checking tune parameters of the vehicles and collection of a bag sample of exhaust gas under varying vehicle operating conditions using a dynamometer. The bag sample was analysed for sulphur compounds by gas liquid chromatography. Even when the tests were refined on the basis of experience, it was not possible to correlate "smelliness" with specific operating conditions.

At this stage the then Department of Arts, Heritage and Environment agreed to fund a cooperative project between the SPCC

and the CSIRO Division of Fossil Fuels to measure the emission of reduced sulphur from catalyst-equipped vehicles on a real time basis in order to determine the operating conditions responsible for odour emission.

2. EXPERIMENTAL TECHNIQUES

2.1 Vehicle Test Procedures

The production of reduced sulphur compounds in exhaust gas was studied in sixteen vehicles (Table 1). Also listed in the table are the catalyst system, odometer reading and date of manufacture for each vehicle. Because smelly exhausts are associated with periods of acceleration or deceleration, a standard urban drive cycle such as ADR 27 was not appropriate for these investigations. Consequently the test cycle finally devised consisted of the following:

    30 s idle
    30 s 40 kph
    30 s 80 kph
    30 s 120 kph
    120 s idle
    120 s 40 kph
    120 s 80 kph
    120 s 120 kph
    30 s idle
    30 s 40 kph
    30 s 80 kph
    30 s 120 kph

In addition some tests were carried out using the following cycle:

    150 s 120 kph
    120 s idle
    300 s 120 kph
    120 s idle
    600 s 120 kph

Acceleration to a new speed was performed at 1.85 m/s^2, whilst deceleration was carried out as rapidly as possible without locking the wheels.

In certain vehicles it was feasible to insert thermocouples (chromel-alumel) into the catalyst matrix and the exhaust pipe upstream of the catalyst.

It had been hoped to test a catalyst whose surface coating was designed to minimise the extent of sulphur storage (through chemical reaction with SO_2 during oxidising conditions); unfortunately the catalyst assembly did not arrive within the time-scale of this project.

2.2 Analytical Procedures

2.2.1 Exhaust gas analysis

The vehicle test cell layout is shown in Figure 1 and the apparatus for determining the reduced sulphur content of the exhaust gas is shown schematically in Figure 2.

A sample of the exhaust gas was drawn off continuously at a rate of approx. 20 L/min and passed through a cooler to remove the bulk of the water vapour. A portion of this cooled sample gas (usually 1 L/min) was was passed through a SO_2 denuder tube before being diluted twentyfold with laboratory air. The separation of reduced sulphur compounds from SO_2 was similar to the procedure of de Souza and Bhatia (1976) except that a diffusion tube rather than a packed bed absorber was used. The denuder tube consisted of a $NaHCO_3$ coated glass tube 400 mm x 6 mm id. The tube allowed no detectable SO_2 to pass through when the input stream contained 10 ppm SO_2. The dilution was necessary not only to keep within the dynamic range of the sulphur analysers but also because the analysers are designed to measure volatile sulphur compounds in air. Two sulphur analysers (Columbia/Meloy total sulphur meter type SA 160) were employed, one to measure total reduced sulphur compounds (TRS), the other for organic sulphur compounds. A portion of the diluted SO_2-free sample gas was drawn off by each

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analyser, one stream passing through a second denuder tube coated with lead acetate to remove H_2S thereby only recording organic sulphur; the other detector measured the total reduced sulphur content. The detectors were calibrated with COS and H_2S calibration mixtures supplied by CIG. The calibration gases, containing 10.5 ppm COS or 18.5 ppm H_2S, were introduced at a known flowrate into the dilution vessel.

Other components of the exhaust gas - CO_2, CO, hydrocarbons(HC) and NO_x - were continuously analysed using standard techniques (non-dispersive infrared analysis for CO, CO_2 and HC; chemiluminescence for NO_x). The exhaust was diluted with make-up air to give a constant volumetric flowrate ($10 \text{ m}^3/\text{min}$) before analysis. One short-coming was that during periods of rapid acceleration, the CO concentration frequently exceeded the dynamic range of the CO monitor.

The outputs from the sulphur analysers and the thermocouples were recorded on a strip-chart recorder. The outputs from the gas analysers were recorded on a second strip-chart recorder. In order to facilitate subsequent data analysis, speed, CO_2, CO, HC, TRS, COS, and when measured, the catalyst temperature (T_{cat}) and the upstream exhaust temperature (T_{up}) were recorded on an eight-channel 8 bit data logger. (Owing to an intermittent software fault associated with the directory of the resulting ASCII files, not all runs were successfully logged.)

2.2.2   Fuel sulphur contents

The sulphur content of the fuels in the test vehicles was determined by XRF analysis (Labex) using a ^{55}Fe source. The instrument was calibrated with known solutions of dibutylsulphide in isooctane in the range 0.01 - 0.5% w/w S.

To investigate the influence of fuel sulphur content on emissions of reduced sulphur compounds, standard ULP fuel was doped with dimethylsulphide to yield a range of sulphur contents. Nominally those used in this study were 0.03, 0.06 and 0.12% w/w S, the actual values being 0.029, 0.067 and 0.112% w/w S.

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3. RESULTS AND DISCUSSION

Previous investigations (Cadle and Mulawa, 1978) have shown that the major species of reduced sulphur for automobile exhaust are H_2S and COS, consequently in the following discussion sulphur measured by the organic sulphur analyser is assumed to be COS.

A typical set of measurements from a test cycle is shown in Figure 3, where eight parameters - speed, CO_2, CO, HC, TRS and COS concentrations, and catalyst and upstream exhaust temperatures - were logged.

A summary of the test results is given in Table 2, which lists the peak emissions of TRS and COS measured during the test cycle, along with the relationship of the peak to the drive cycle, i.e. whether the emissions occurred during acceleration or deceleration, and the transition speed range. The sulphur contents of the fuel used in the test are also listed. In many cases, a particular car was re-tested with the air pump disconnected from the exhaust or the car was made to run rich (i.e. reducing conditions in the exhaust gas) by connecting a suitable resistor (usually 500 ohm) in place of the water temperature sensor. Frequently, disconnecting the air pump reduced the peak values and the emissions were spread over a wider part of the drive cycle. Emissions during acceleration were highest for the transition 80 - 120 kph. Only two vehicles in standard condition emitted the highest values during deceleration, viz. the Turbo Commodore and a Toyota Corona, which are discussed later.

Four vehicles were used to examine further the influence of fuel sulphur contents. Detailed analysis of these data highlighted the influence of catalyst temperature, CO and HC concentrations, as well as fuel sulphur levels. On two occasions, emissions of TRS and COS were observed to vary with catalyst temperature at a time when other parameters such as CO and HC concentrations were substantially constant. The data are shown in Figures 4 and 5. The first instance (Fig. 4) concerns emissions from ODN-851 during

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an idle period when the vehicle was adjusted to run rich by inserting a 1000 ohm resistor in place of the water temperature sensor. The second occasion (Fig. 5) was for ZCD-818 during a 120 kph cruise period, a speed at which the car produced, in normal configuration, a reducing exhaust gas mixture. It can be seen that the emissions of TRS and COS are a strong function of temperature. This is consistent with the measurements of Cooper et al. (1986) who observed that the H_2S emissions from a laboratory Pt/Rh catalyst during steady state operation nearly doubled when the temperature was increased from 550 to 600°C.

The level of reduced sulphur emissions was also found to be a function of the concentration of CO in the exhaust gas. This is shown in Figure 6 for emissions from ZCD-818 for two fuel sulphur contents. These data are for substantially constant temperatures (585 + 10)°C for the 0.06% S fuel and 610°C for the 0.03% S fuel.

The effect of CO on emissions from the lower sulphur content fuel is not discernible due to the small spread in the data. However, the data do lie below those for the higher S fuel.

Reduced sulphur emissions rose with increasing fuel sulphur content as demonstrated to some extent in Figure 6 but more clearly in Figures 7 to 10, where the peak values of TRS emitted when accelerating from 80 to 120 kph are plotted as a function of fuel sulphur content for two vehicles with three-way catalysts, ODN-851 and ZCD-818, and two with oxidation catalysts, ZUO-425 and ZUL-103. The three episodes of acceleration in the test cycle are identified. For the second and third accelerations the TRS values increased with fuel S content; the emissions from the first acceleration period were more erratic as the catalyst had not reached its usual temperature range. In Figure 10, the emissions from the 0.06% S fuel were not significantly different from those from the 0.03% S fuel. This is probably due to the lower precision of the sulphide concentration measurements at these low emission levels. The increased emissions at 0.12% S are significant. The reason for the difference in peak emissions between the two Mitsubishi Colts ZUO-425 and ZUL-103 is unknown.

These observations are consistent with the measurements of Cooper et al. (1986) who also observed a rise in H_2S emissions with increasing fuel sulphur levels when operating a Pt/Rh catalyst under steady conditions. Their data indicated that the H_2S emissions initially increased a little more rapidly than the corresponding input sulphur. Only the data for ZCD-818 show this effect, however, the natural variation between different tests, particularly if different drivers were used, may mask this effect.

The possibility of sulphur storage by the catalyst has been discussed by Trimm (1987) and Cooper et al. (1986). This occurs when some of the components of the catalyst surface are converted to "catalyst sulphate" by SO_2 in the exhaust gas under oxidising conditions. When a burst of reducing conditions passes through, typical of hard acceleration, both the catalyst sulphate and SO_2 are reduced to TRS. The experiments carried out in this study did not, in general, lend themselves to detailed analysis of this phenomenon, largely because CO levels exceeded the capacity of the CO analyser. Thus it was not possible to unravel the combined effects of catalyst temperature and the extent of reducing conditions (i.e. CO concentration). However the reduction of peak emissions when the exhaust gas control system was interfered with to produce rich conditions suggests that catalyst storage does take place.

From Table 2 it can be seen that one car in particular (Toyota Corona NZH-676) emitted TRS only during periods of deceleration. The noteworthy feature of this vehicle was that it produced higher levels of NO_x than other vehicles during the cruise part of the cycle, suggesting that the exhaust gases were in general more oxidising than for other vehicles. Although reducing conditions did prevail during acceleration, no significant levels of TRS were produced on these occasions. Another feature was that the emissions largely comprised COS.

Other vehicles which emitted significantly on deceleration were those that tended to run rich in "on-road" condition (the Turbo Commodore and NZQ-487), ODN-851 when adjusted to run rich,

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and ZCD-818 which tended to run rich at high speed. Although the exhaust characteristics of these vehicles were reducing rather than oxidising, the proportion of COS was again much higher than for acceleration. Replacing the Turbo Commodore's catalyst with that from ODN-851 produced no significant change to the sulphide emissions, confirming that the nature of the exhaust gas is all important. The only vehicle to emit a high proportion of COS when accelerating was NZQ-487. COS/TRS ratios observed in this study cover the range found by Cadle and Mulawa (1978).

Equilibrium thermodynamic calculations carried out for the C-H-O-N-S system indicate that the proportion of TRS present as COS should be less than 5% as indicated in Figure 11, which presents the results of such calculations as a function of temperature and air-fuel ratio. In Table 2 it can be seen that during acceleration about 10% of TRS is COS for the higher level emissions associated with the higher sulphur fuels. However much higher proportions were associated with deceleration which must be a consequence of the kinetics of the chemical reactions concerned.

4. CONCLUSIONS

(1) Emissions of reduced sulphur compounds by catalyst-equipped vehicles occur only when

    (a) reducing conditions exist in the exhaust gas, and

    (b) catalyst temperature is higher than 250 – 300°C.

(2) Excursions into reducing conditions occur during periods of strong acceleration or deceleration, largely the former.

(3) TRS emissions increase with stronger reducing conditions in the exhaust gas.

(4) TRS emissions increase with increasing fuel sulphur content.

(5) Sulphur storage due to the formation of catalyst sulphate probably occurs.

(6) For high levels of TRS (from high S fuels) emitted during periods of acceleration, COS usually constitutes about 10%. However during deceleration COS is the major component.

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With the catalytic converter technology currently in use in Australia, rich excursions in exhaust gas composition are difficult, if not impossible, to prevent during hard acceleration or high speed cruising and catalyst temperatures usually exceed $400^{\circ}C$. Consequently, the only substantial control over the intensity of reduced sulphur emissions would appear to be through limiting the sulphur content of the fuel.

However, if sufficient air were pumped into the exhaust, the rich excursions could be eliminated. This methodology was used in the USA in the 1970s and early 1980s, although the current trend in that country is towards catalytic converters similar to those used in Australia.

5. ACKNOWLEDGEMENTS

6. REFERENCES

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Cooper,B.J.,Truex,T.J. and Chapman, P.R., 1986. H_2S emissions from catalyst equipped vehicles. Paper presented at 7th World Clean Air Congress, Sydney, Australia.

De Souza, T.L.C. and Bhatia, S.P., 1976. Developement of calibration systems for measuring total reduced sulfur and sulfur dioxide in ambient concentrations in the parts per billion range. Anal. Chem., 48, 2234-40.

Trimm, D.L., 1986. Odour production in catalyst-equipped cars. Report to the SPCC from the Department of Chemical Engineering, University of New South Wales.

Trimm, D.L., 1987. The case of the smelly cars. Chem. Aust., 54(3), 85-6.

TABLE 1. LIST OF TEST VEHICLE DETAILS

Vehicle	ID	Catalyst system†	Odometer (km)	Date of manufacture
Ford Falcon 4.1 L	NWO-276	OC + PA	33220	1/86
Holden Commodore Turbo	8K198G J119882*	TWC + FI	110	12/86
Ford Fairlane	C-337	OC + FI + PA	60402	1/86
Toyota Corona	ZUK-195	OC + AP	21351	2/86
Mitsubishi Colt	ZUN-150	OC + PA	3420	11/86
Toyota Tarago 2.0 L	YR210054812	TWC + PA	90	3/87
Toyota Corona	ZUN-011	OC + PA	3300	10/86
Mitsubishi Colt	ZUL-154	OC + PA	10531	8/86
Mitsubishi Colt	ZUM-774	OC + PA	38	2/87
Mitsubishi Colt	ZUN-166*	OC + PA	70	12/86
Toyota Cressida	NRR-734	TWC + FI	22530	9/85
Ford Falcon 4.1 L	SIDO 620263	OC + PA	12582	7/86
Mitsubishi Colt	ZUO-425*	OC + PA	39	5/87
Mitsubishi Colt	ZUL-103*	OC + PA	19344	7/86
Holden Commodore	OLV-128	TWC + FI	35	4/87
Holden Commodore	ODN-851*	TWC + FI	7376	8/86
Ford Falcon 3.3 L	OBS-768	OC + PA	8952	7/86
Ford Falcon 4.1 L	NZR-379	OC + PA	29900	5/86
Mitsubishi Sigma	NYJ-557	OC + PA	16600	4/86
Ford laser 1.6 L	NZQ-487*	OC + PA	12700	4/86
Toyota Corona	NZH-676*	OC + AP	15000	4/86
Holden Commodore	ZCD-818*	TWC + FI	36700	8/86

* Vehicles more intensively investigated.

†OC - Oxidation catalyst, PA - Pulse air injection system, AP - Air pump air injection system,
TWC - Three-way catalyst, FI - Fuel injection.

TABLE 2. PEAK REDUCED SULPHIDE EMISSIONS (ppm) FROM TEST VEHICLES

Vehicle	ID	Other conditions	Fuel S(%w/w)	Peak TRS and Corresponding COS					
				Acceleration		Speed (kph)	Deceleration		Speed (kph)
				TRS	COS		TRS	COS	
Turbo Comm	8K198GJ119882		0.02	2.30	0.60	80–120	2.00		80–40
		SPCC CAT*	0.02	2.50	0.50	80–120	3.70	2.60	80–40
Falcon	NWO-276			No significant emissions					
Toy Corona	ZUK-195		0.02	0.50	0.5	80–120	–	–	–
		Air off	0.02	1.00	1.00	"	–	–	–
Mitsu Colt	ZUN-150		0.01	0.40	0.40	"	–	–	–
		Air off	0.01	0.20	0.20	"	–	–	–
Ford F/L	C-337		0.01	0.50	–	"	0.50	–	120–80
Toy Tarago	YR210054812		<0.01	1.00	0.40	"	–	–	–
		Air off	<0.01	0.20	0.20	"	–	–	–
Toy Corona	ZUN-011		<0.01	No significant emissions					
		Air off	<0.01	–	–	–	0.60	0.60	120–80
			0.03	0.30	0.06	80–120	–	–	–
			0.03	–	–	–	1.60	0.80	120–80
Mitsu Colt	ZUL-154		0.01	0.16	0.10	80–120	–	–	–
		Air off	0.01	0.12	0.10	"	0.12	0.06	120–80
Mitsu Colt	ZUN-166		<0.01	0.10	0.04	"	–	–	–
		Air off	<0.01	0.16	0.10	"	–	–	–
Toy Corona	NZH-676		0.03	–	–	–	1.00	1.00	80–40
		Air off	0.03	–	–	–	1.60	1.60	"
			0.12	–	–	–	6.00	6.00	"
		Air off	0.12	–	–	–	2.00	2.00	"
			0.06	–	–	–	3.00	2.80	"
		Air off	0.06	–	–	–	2.00	1.50	"
Laser 6% CO†	NZQ-487		0.03	1.00	0.80	80–120	–	–	–
		Air off	0.03	1.00	0.80	"	2.80	2.80	120–80
			0.12	3.60	3.20	"	2.80	2.80	"
		Air off	0.12	3.60	.20	"	5.60	5.20	"
Laser 1.5% CO†	NSQ-487		0.12	4.40	4.40	"	–	–	–
		Air off	0.12	3.60	3.20	"	2.40	2.50	120–80
			0.06	1.20	1.20	"	1.60	1.20	"
Toy Cressida	NRR-734		0.02	0.90	0.80	"	0.60	0.50	"
		500 ohm	0.02	1.80	0.80	"	0.70	0.50	"
			0.02	0.90	0.80	"	0.90	0.80	"
Holden Com	ODN-851		0.12	12.00	1.20	"	1.60	1.20	"
		500 ohm	0.12	9.00	1.00	"	16.00	8.00	"
			0.12	12.00	1.30	"	0.90	0.30	"
		500 ohm	0.12	13.00	1.40	"	0.90	–	–
			0.06	10.00	0.80	"	0.50	0.20	120–80
			0.03	6.00	0.60	"	0.60	–	–
Mitsu Colt	ZUO-425		0.06	6.40	1.60	"	–	–	–
			0.03	2.20	0.60	"	–	–	–
			<0.01	0.60	0.40	"	–	–	–
Mitsu Colt	ZUL-103		<0.01	0.30	0.30	"	0.60	0.50	120–80
			0.03	0.30	0.30	"	–	–	–
			0.06	1.10	0.80	"	–	–	–
Holden Com	ZCD-818		0.03	3.00	1.00	"	1.10	0.60	120–80
			0.06	4.00	1.00	"	3.70	0.40	"
			0.12	10.00	0.80	"	–	–	–

* This test involved replacing the original catalyst with that from ODN-851.
† CO exhaust concentration at idle.

FIG. 1 VEHICLE TEST CELL LAYOUT

DILUTION AIR INLET

SAMPLING VENTURI

CRITICAL FLOW VENTURI

CYCLONIC SEPARATOR

BLOWER

SAMPLE LINE

TO ANALYSER TRAIN

TO SULPHIDE ANALYSIS EQUIPMENT
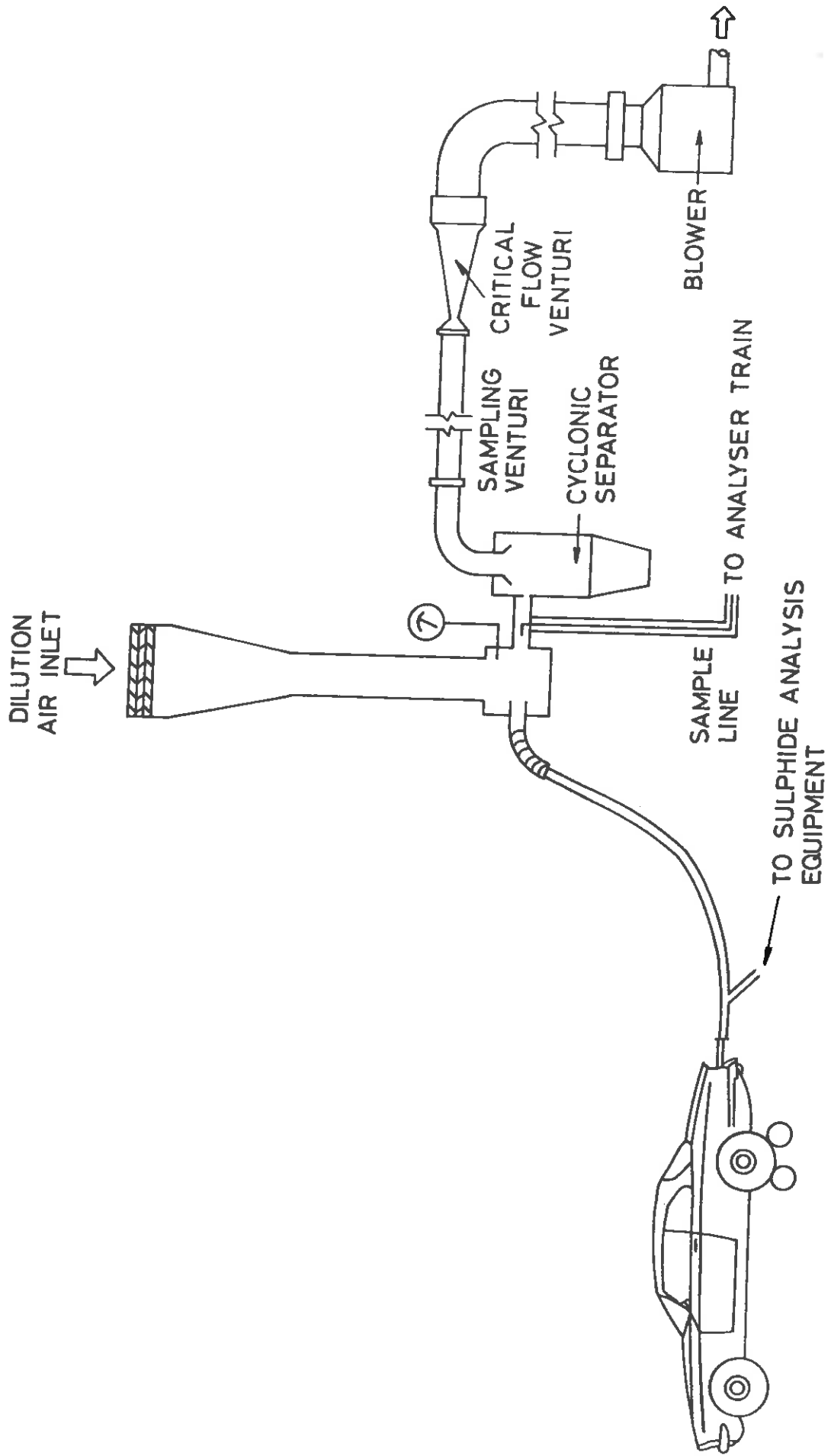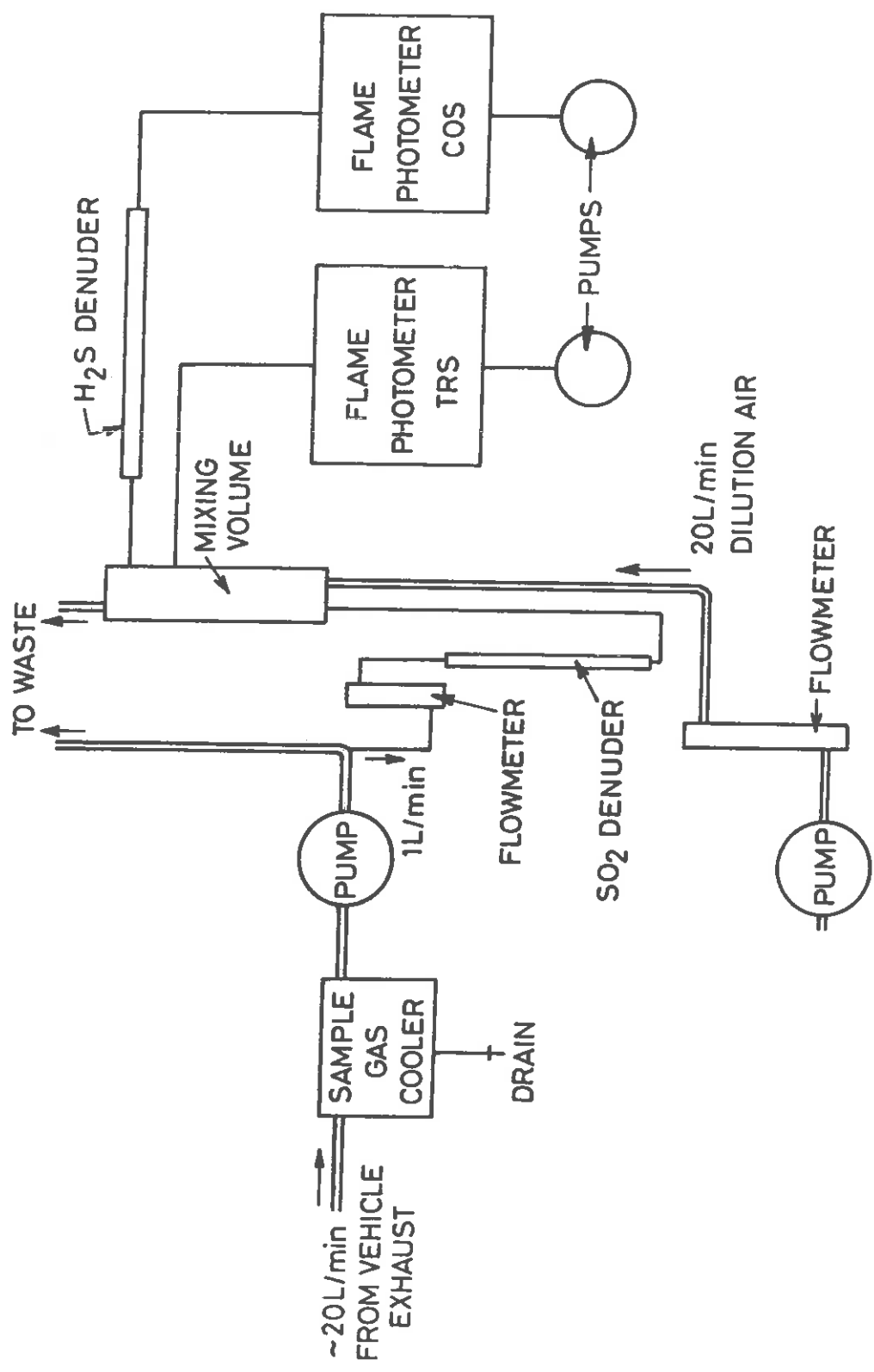
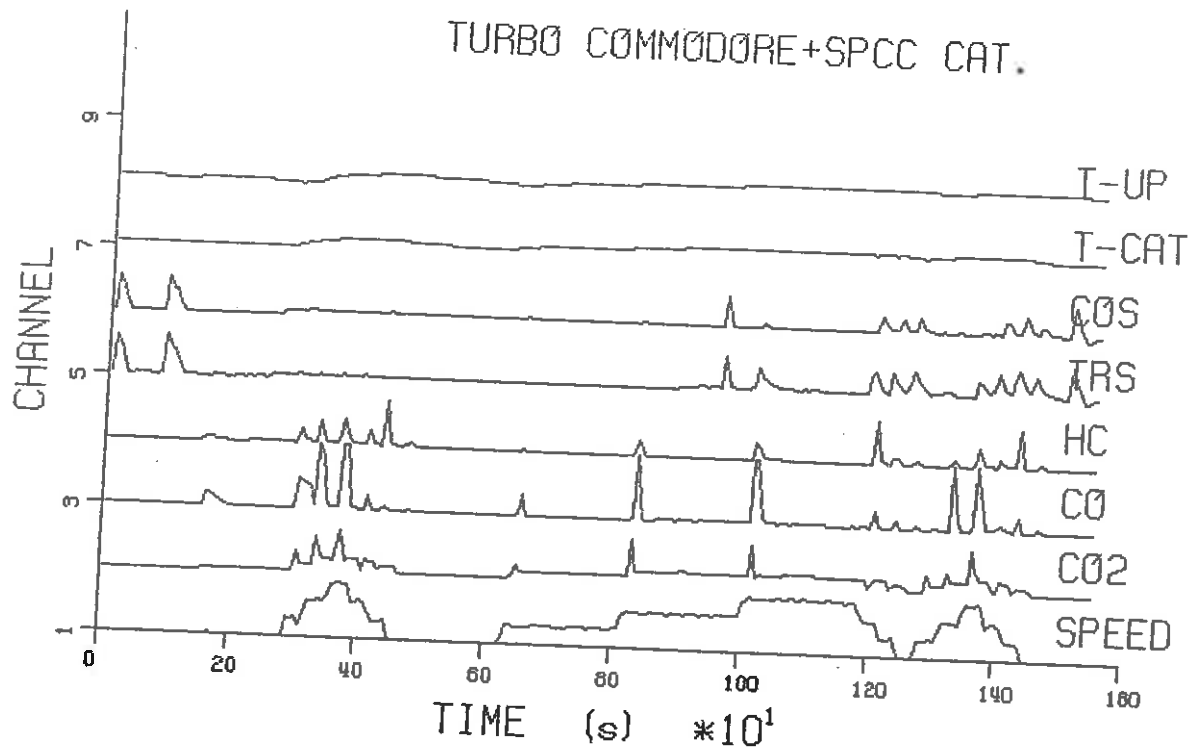FIG. 2 SCHEMATIC DIAGRAM OF APPARATUS FOR MEASURING REDUCED SULPHUR COMPOUNDS

FIG. 3   TYPICAL RESULTS FROM TEST CYCLE FOR EIGHT PARAMETERS –
SPEED, CONCENTRATIONS OF CO_2, CO, HC, TRS, COS AND CATALYST
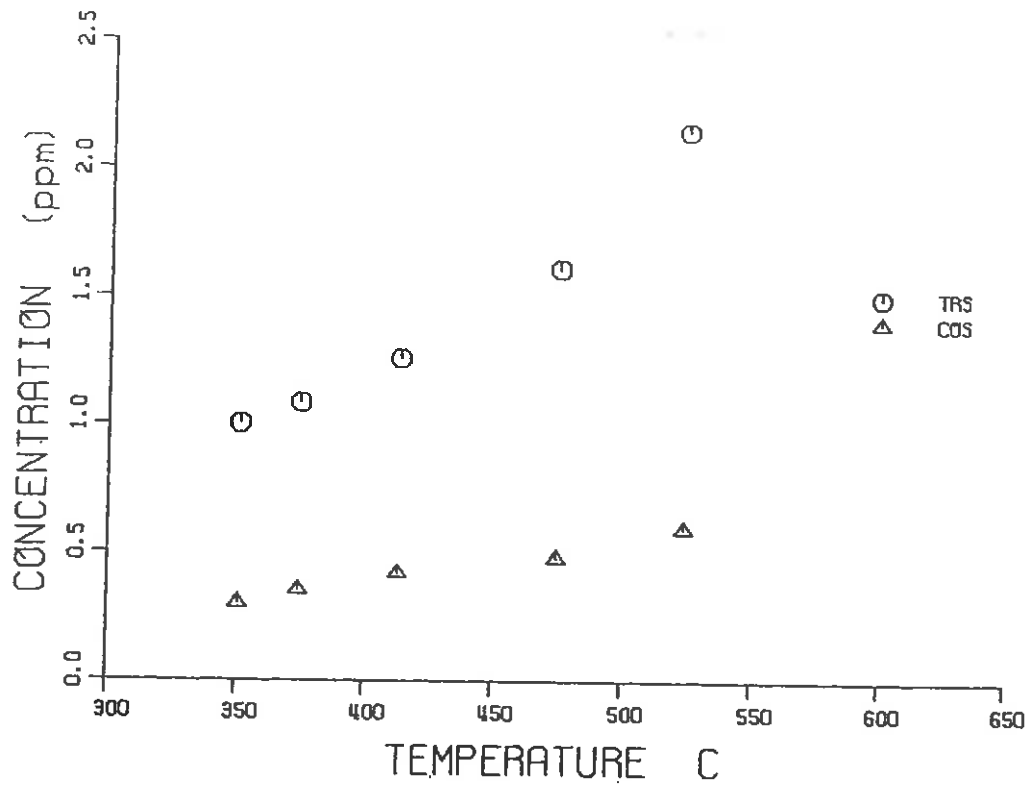AND UPSTREAM EXHAUST TEMPERATURES.

FIG. 4   CONCENTRATIONS OF TRS AND COS AS A FUNCTION OF
TEMPERATURE FOR ODN-851 DURING AN IDLE PERIOD (FUEL S
CONTENT 0.12% w/w).
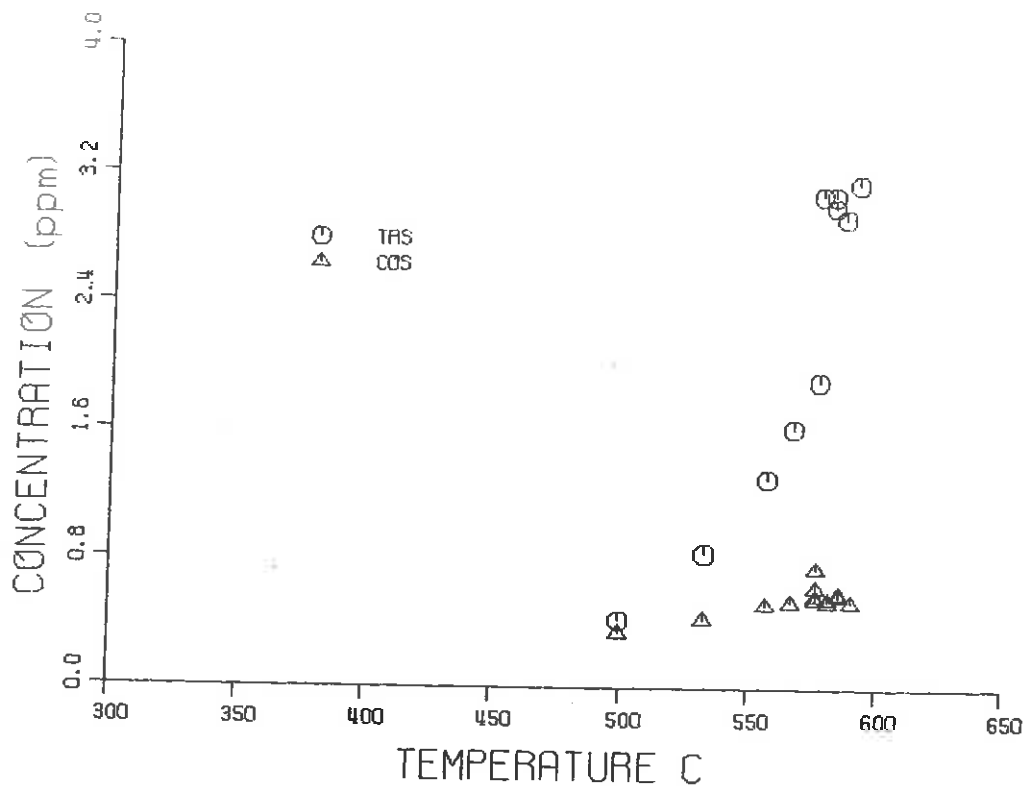
FIG. 5   CONCENTRATIONS OF TRS AND COS AS A FUNCTION OF
TEMPERATURE FOR ZCD-818 DURING A 120 kph CRUISE PERIOD
(FUEL S CONTENT 0.06% w/w).
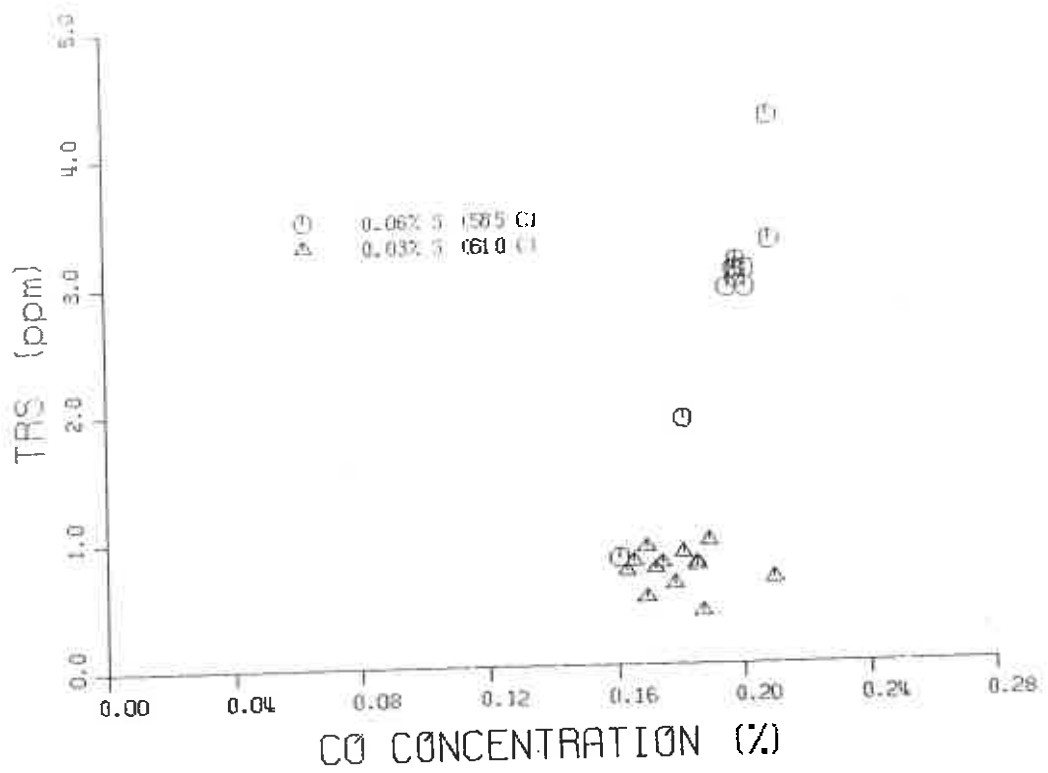
FIG. 6   TRS EMISSIONS AS A FUNCTION OF CO CONCENTRATION AT
CONSTANT TEMPERATURE (ZCD-818).
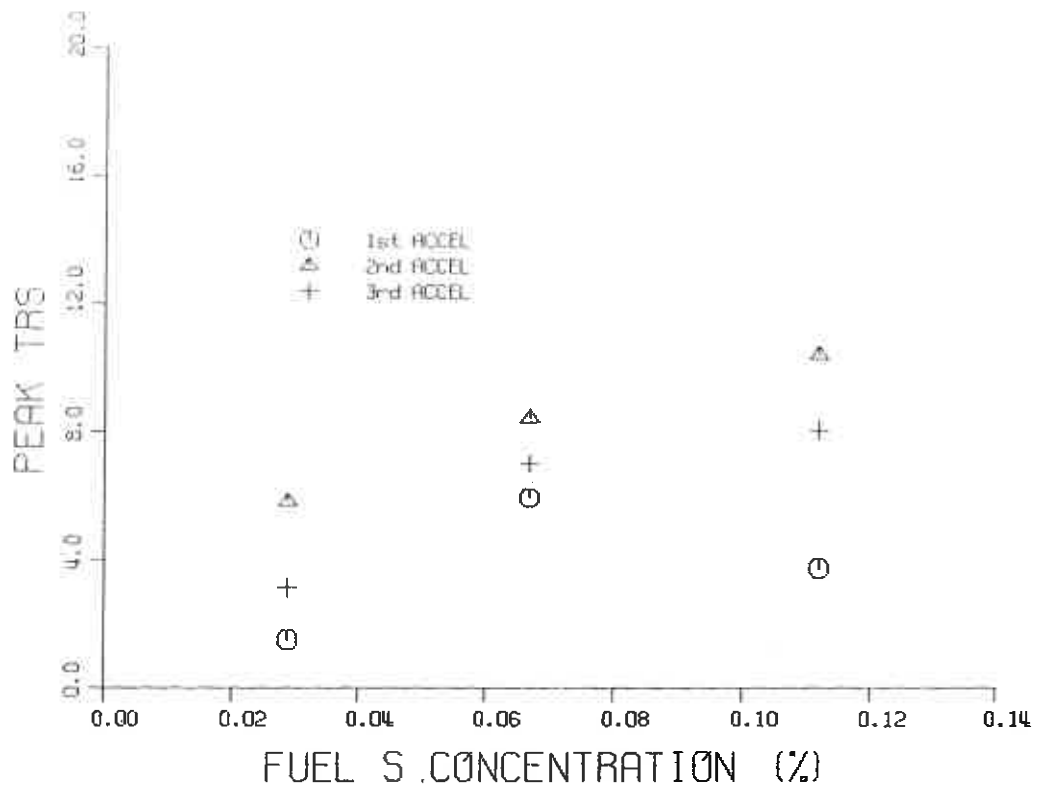
FIG. 7   PEAK TRS EMISSIONS (ppm) AS A FUNCTION OF FUEL SULPHUR
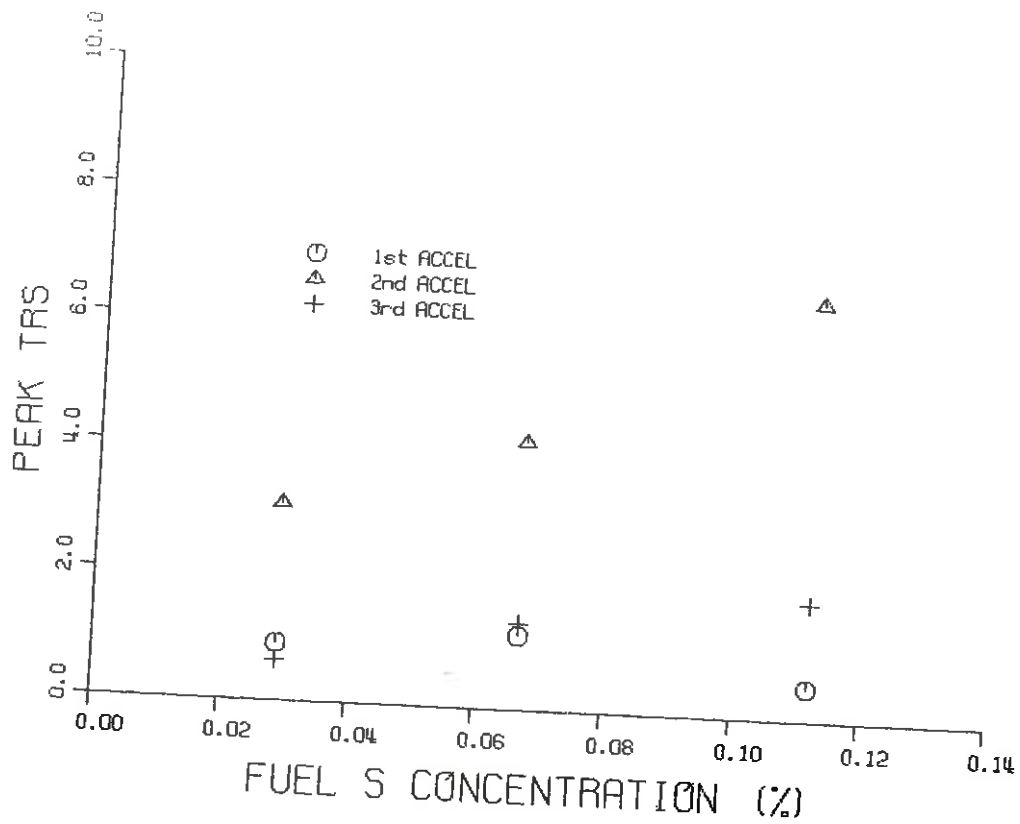CONTENT FOR THE 80 - 120 KPH ACCELERATION PERIOD (ODN-
851).

FIG. 8   PEAK TRS EMISSIONS (ppm) AS A FUNCTION OF FUEL SULPHUR
          CONTENT FOR THE 80 - 120 KPH ACCELERATION PERIOD (ZCD-
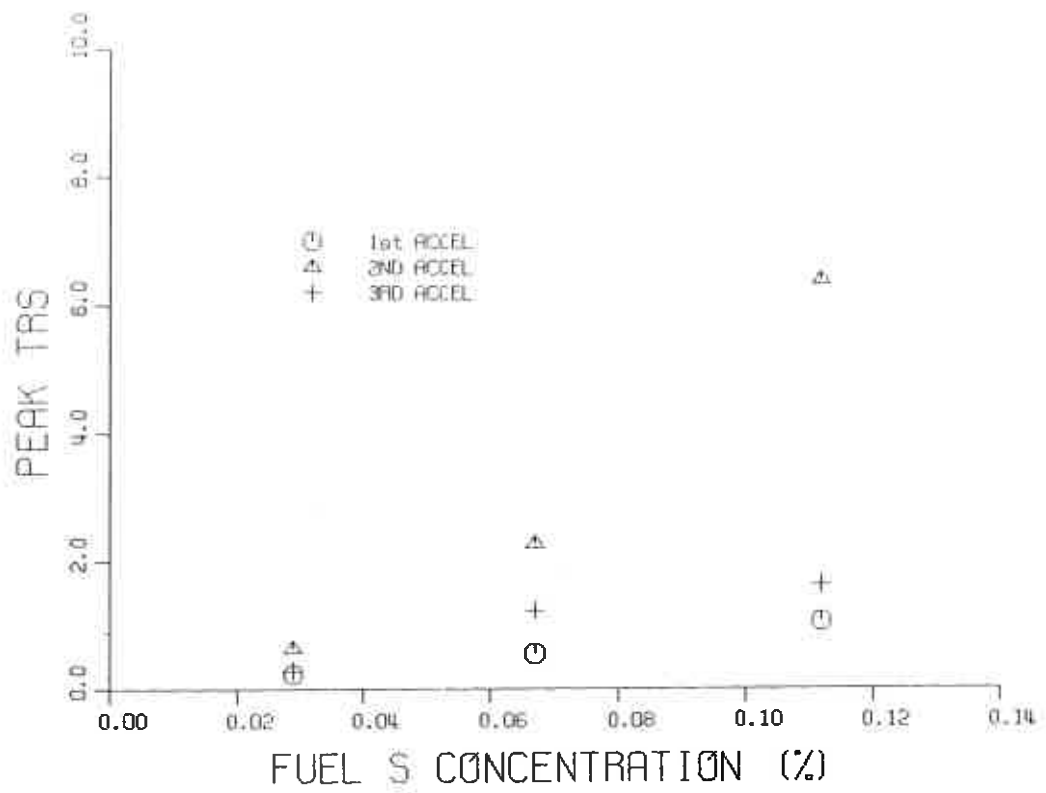   818).

FIG. 9   PEAK TRS EMISSIONS (ppm) AS A FUNCTION OF FUEL SULPHUR
CONTENT FOR THE 80 - 120 kph ACCELERATION PERIOD (ZUO-
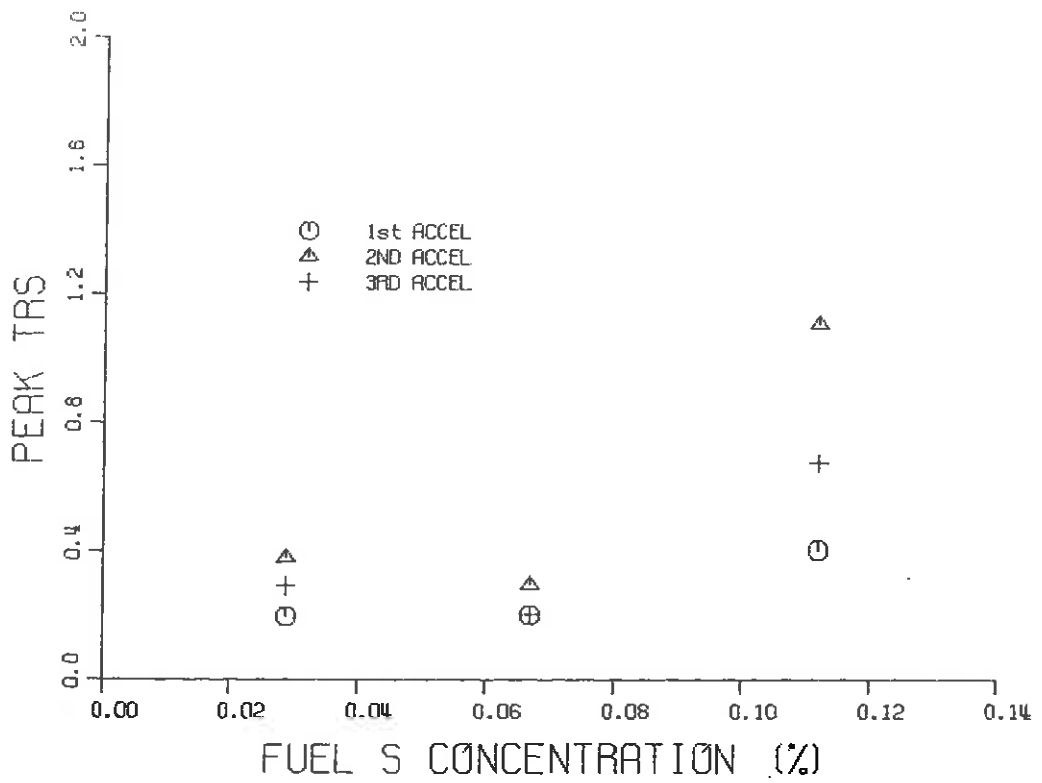425).

FIG. 10   PEAK TRS EMISSIONS (ppm) AS A FUNCTION OF FUEL SULPHUR
           CONTENT FOR THE 80 - 120 kph ACCELERATION PERIOD (ZUL-
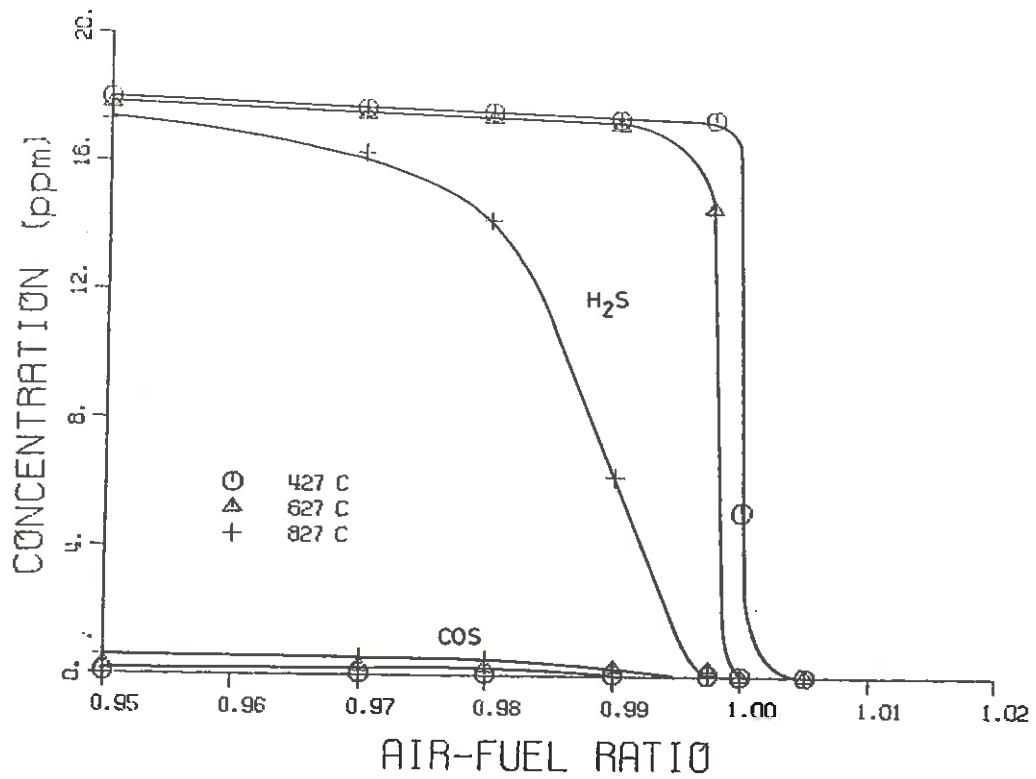   103).

FIG. 11   CALCULATIONS OF EQUILIBRIUM THERMODYNAMIC
CONCENTRATIONS OF H_2S AND COS AS A FUNCTION OF
TEMPERATURE AND AIR-FUEL RATIOS (FUEL S CONTENT 0.03%
W/W.