

**Ambient Hydrocarbon Air Quality Monitoring Network
Audit Report**

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July 1998

NPL Report COEM 12

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ISSN COEM - 1369 6807

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Approved on behalf of Managing Director, NPL
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AMBIENT HYDROCARBON AIR QUALITY MONITORING NETWORK AUDIT REPORT

1. INTRODUCTION

Hydrocarbon Network site audit visits were carried out between November 1997 and February 1998 with the exception of Marylebone road which was audited in March 1998. The complexities of this new site mean that some results are still being analysed. The schedule of audit visits is given in table 1.

Table 1 Audit visit schedule

Site Name	Date of Audit	Auditor
Belfast	10/12/97	R Robinson
Birmingham	08/01/98	R Robinson
Bristol	02/12/97	R Robinson
Cardiff	03/12/97	R Robinson
Edinburgh	18/12/97	R Robinson
Eltham	26/11/97	R Robinson
Harwell	10/02/98	D Butterfield
Leeds	16/12/97	R Robinson
Liverpool	08/12/97	R Robinson
London-UCL	27/11/97	R Robinson
Middlesbrough	17/12/97	R Robinson
Southampton	01/12/97	R Robinson
Marylebone Road	18/3/98	R Robinson

The purpose of the visits was to:

- i) Assess the state of repair of the equipment and structure of the sites.
- ii) Audit the performance of the Local Site Operators in carrying out their routine duties.
- iii) Check overall operation of the instrumentation.
- iv) Inject three inter-comparison gas mixtures to check instrument calibration and compare instrument performance.
- v) Request LSO feedback.

2. STATE OF REPAIR OF SITES

The state of repair of all sites was assessed. The table lists all observations made about each site.

Table 2 State of repair of sites

Site Name	State Of Equipment	Structural Repair	Other Observations	Actions
Belfast	LN ₂ Dewar icing up and using high amounts of LN ₂	Good, new doors to garage have been fitted	-	Re-lagged pipework on LN ₂ dewar. Replace LN ₂ dewar - Done - 13/01/98
Birmingham	Good	Good	-	None
Bristol	Hi Volume manifold pump needs attention as cover is loose.	Good	OK, In need of a general clean	Site tidied Action NPL - secure pump cover
Cardiff	H ₂ Generator water level indicator broken - still possible to see water level.	Good	-	None
Edinburgh	Good	Good	-	None
Eltham	H ₂ Generator power light not working. LN ₂ level indicator not working.	Good	One light in room not working, making it hard to see filter state	None
Harwell	Good	Good	-	None
			-	None
Liverpool	Flow meter rubber teats perished.	Good	-	New teat supplied.
London-UCL	FID hard to light after silica gel changed in H ₂ generator	Good	-	None
Middlesbrough	Air conditioner leaks.	Good	-	Fit guttering / drain to air conditioner- ACTION NPL
Southampton	Sample inlet pipe connector hard to remove. LN ₂ exhaust tube needs new fitting	Good	-	Sample inlet pipe replaced during audit. New exhaust fitting sent to LSO.
Marylebone Road	Good	Good	-	None

Connectors were installed by NPL at all sites to allow the site standard delivery pipes to be connected to the bypass when not in use. This seals the calibration delivery tube when not in use, preventing leaks and stopping dust entering the pipework.

3. LSO AUDIT

The LSOs were observed performing their weekly checks and attaching the calibration standard (where applicable).

Table 3 LSO audit.

Site Name	Name of LSO Audited	Weekly Checklist Completed OK	Site Standard applied correctly
Belfast	Grant Smith	✓	✓
		✓	✓
		✓	✓
		✓	✓
	Forrest	✓	✓
		✓	✓
		✓	✓
		✓	✓
Liverpool	Harry Jones	✓	✓
London-UCL	Phil Henderson	✓	N/A
Middlesbrough	Geoff Gray	✓	✓
		✓	✓
		✓	N/A

London-UCL and Marylebone Road use automated standard injection systems and LSOs are not required to manually attach the calibration standards. These LSOs were however required to show they were able to run an automated calibration on request.

The performances of the LSOs were all considered to be to a good standard, with no points of action arising.

The audit visit also provided an opportunity for three new deputy LSOs to be trained at Southampton.

4. ROUTINE OPERATION OF EQUIPMENT

The normal operation of the Chrompack VOC Air Gas Chromatographs, together with the associated ancillary equipment, was observed at the 12 network sites. Various GC parameters were observed during the runs, to ensure the GCs were maintaining the correct pressures and temperatures.

Table 4 GC Temperature Control (all values in centigrade)

Site Name	Tube Cryogenic Temperature	Tube Desorption Temperature	Trap Cryogenic Temperature	Trap Injection Temperature
Belfast	-20	250	-100	126 - 133
Birmingham	-20	250	-100	128-137
Bristol	-20	250	-103	125
Cardiff	-20	250	-94	122-137
Edinburgh	-20	270	-100	125-136
Eltham	-20	250	-100	125
Harwell	-19	250	-101	121
Leeds	-20	250	-100	125 -138
Liverpool	-20	252	-98	125 -141
London-UCL	-21	248	-100	112
Middlesbrough	-20	250	-100	125
Southampton	-20	250	-103	117
Marylebone Road	n/a	n/a	n/a	n/a

Table 5 Flows and pressures

Site Name	Pump Sample Flow	Sample Flow	Pump Vacuum	Hydrogen generator pressure	Compressor operating	LN ₂ Pressure
Belfast	9.9	11.1 ±0.1	-0.89	2.0	✓	20
Birmingham	9.9	12.3 ±2.0	-0.86	2.0	✓	18
Bristol	9.8	12.1 ±0.3	-0.90	2.1	✓	12
Cardiff	9.8	12.3 ±0.3	-0.90	2.1	✓	11
Edinburgh	9.9	11.0 ±0.1	-0.90	2.0	✓	42 ¹
Eltham	10.0	12.5 ±0.1	-0.90	2.1	✓	16
Harwell	15.0	15.3 ±0.4	-0.92	1.8	✓	12
Leeds	9.8	13.0 ±3.0	-0.91	1.4	✓	11
Liverpool	9.8	10.8 ±0.2	-0.91	2.3	✓	19.5
London-UCL	10.0	-	-0.91	2.0	✓	9
Middlesbrough	9.8	11.3 ±0.2	-0.88	1.9	✓	20
Southampton	9.9	12.2 ±0.2	-0.84	1.8	✓	21
Marylebone Road	n/a	n/a	n/a	n/a	n/a	n/a

¹ this dewar is shared with the university department and maintains a higher operating pressure.

No anomalous instrument behaviour was observed.

5. INTERCOMPARISON GAS INJECTION

5.1 12 EXISTING NETWORK SITES

Three inter-comparison gas mixtures were injected at each site, together with a set of calibration runs using the on-site standard. The mixtures brought by NPL were as follows :

- i) Audit standard : a cylinder of standard gas similar to those used at the sites, used to check the values and application of the on site standard concentrations.
- ii) Ambient air : a cylinder containing a sample of ambient air collected at NPL, used to inter-compare the chromatography of the site GC's.
- iii) Blank cylinder : a cylinder containing freeze dried nitrogen, containing negligible amounts of hydrocarbons, used to check for internal sources of hydrocarbons at each site.

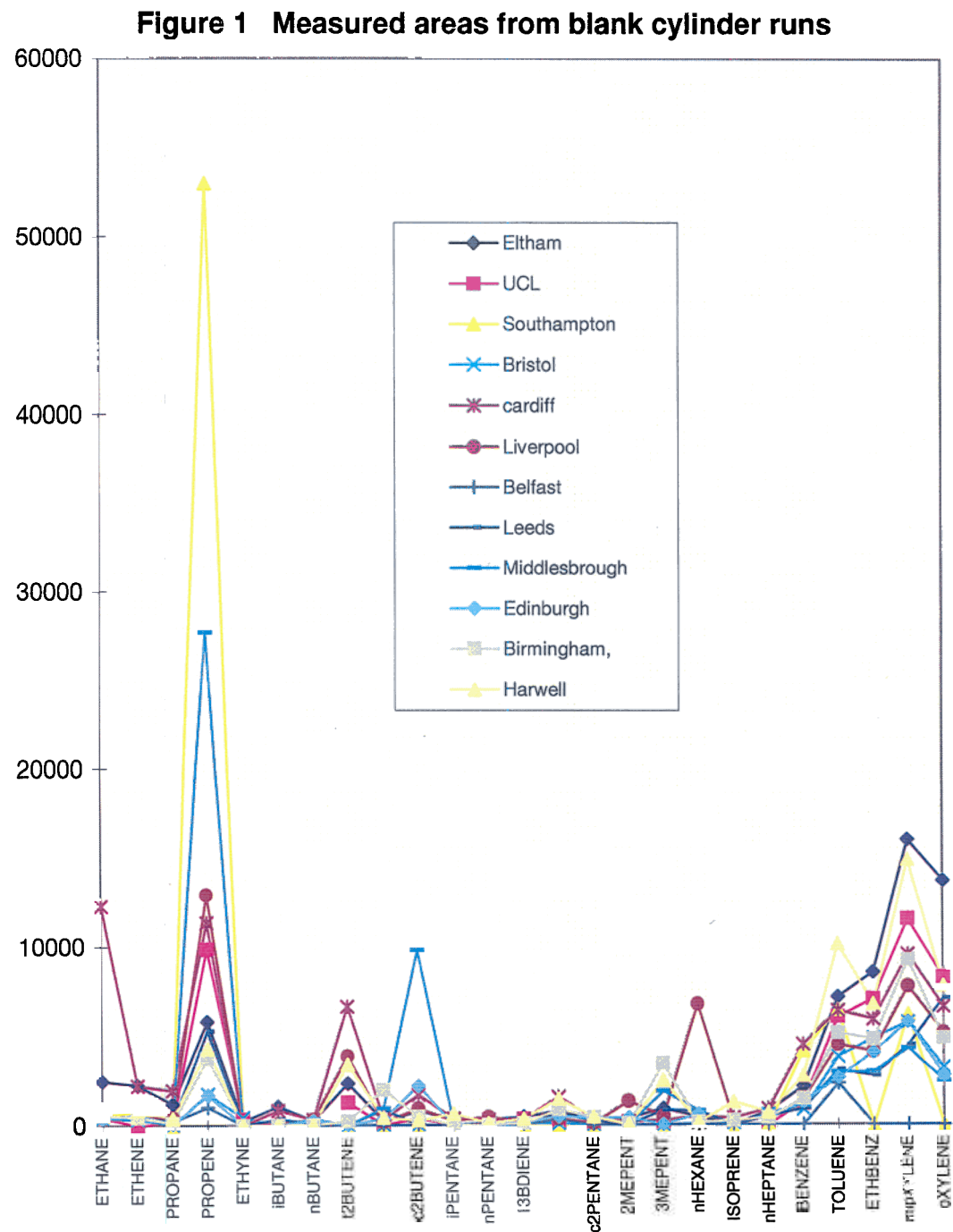
The three cylinders were attached to an automated valve box which was connected to the input of the GC in the same manner as the site standard. The valve box was used overnight to sequentially inject four hours of each gas into the GC, with one void hour between each set. The order of the injections was blank, ambient and audit standard. This was to avoid any carry over or memory effects.

As a part of the LSO audit a site standard calibration was performed. This was used to derive the response factors for the site in the same way as for the regular fortnightly calibration. These response factors were then applied to the results of the ambient and audit standard and the concentrations calculated.

The blank runs were used to determine any internal sources. These internal levels were subtracted from all areas in the inter-comparisons, giving 'blank corrected' response factors and concentrations.

5.1.1 Blank injection

Figure 1 shows the measured areas from the blank runs performed at each site.

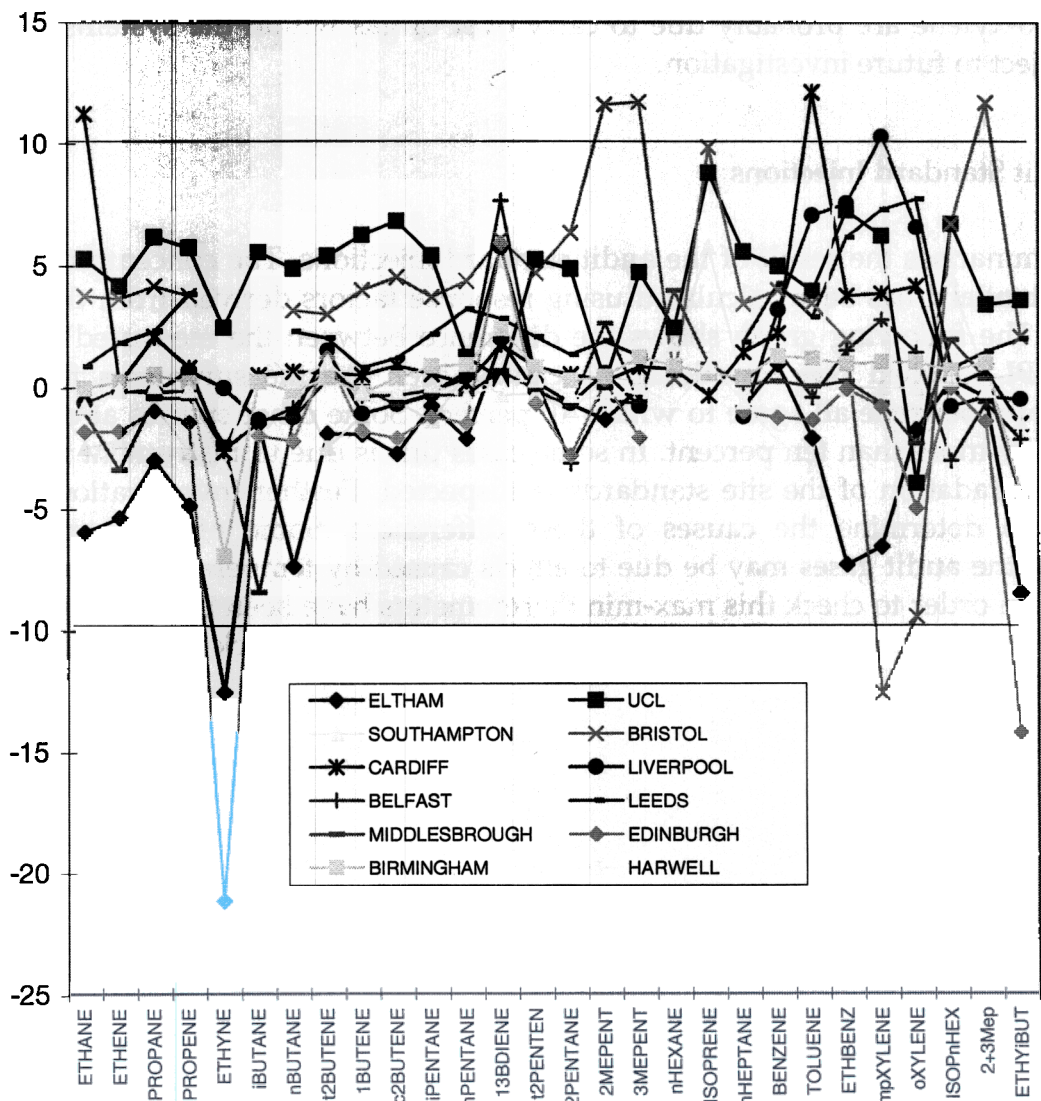


As can be seen from the above graph the most significant internal source at most sites was propene. The areas correspond to concentrations up to approximately 27 ppb at Southampton, though in most cases they are much smaller. These internal sources, which vary with time, have meant that for much of 1997 it has not been possible to ratify propene at Southampton and Middlesbrough. Some sites had small internal sources of benzene, however these had a negligible effect on the ambient concentrations. The apparent internal sources of the compounds from toluene to o-xylene are probably due to carry over of gas within the systems. This will be subject to future investigation.

5.1.2 Audit Standard Injections

Figure2 summarises the result of the audit standard injections. The concentration of the audit standard has been calculated using response factors derived from the site standards. The following graph shows the difference between the measured value and the NPL labelled concentrations. As can be seen the measurements for 1,3 butadiene and benzene all agree to within 10 percent. Some other species at certain sites differ by more than ten percent. In some cases this is due to instrument faults, in others degradation of the site standards is suspected. Further investigations are underway to determine the causes of these differences. Some of the variation observed in the audit gases may be due to effects caused by temperature variations at the sites. In order to check this max-min thermometers have been installed at each site and LSOs asked to monitor them as a part of the weekly check and calibration procedures.

Figure 2 Percentage difference of measured audit standard from NPL value (Blank corrected).



5.1.3 Ambient air injections

The results of the ambient cylinder inter-comparison are used to investigate issues with the chromatography at the sites. These data allow the response of the instrument at ambient concentrations to be inter-compared. The results have clarified issues regarding the elution order of nearly-coeluted ethyne and i-butane. These two species are hard to label as they have similar areas in the calibration standard, and can change elution order. This had been investigated previously by injecting an ethyne standard into the Eltham and Harwell instruments. These earlier tests had confirmed the historically assumed elution orders for ethyne and i-butane. However at some of the sites this has appeared to have altered since annual servicing. This change was evident during ratification from qualitative analysis of the ambient data. In this analysis the i-butane is assumed to be more highly correlated with the n-butane than with the ethyne. Plots of i-butane concentrations against n-butane concentrations can therefore be used to check the identification of these species. The following exemplar figures show this effect.

Figure 3 Correlation of n-butane to ethyne

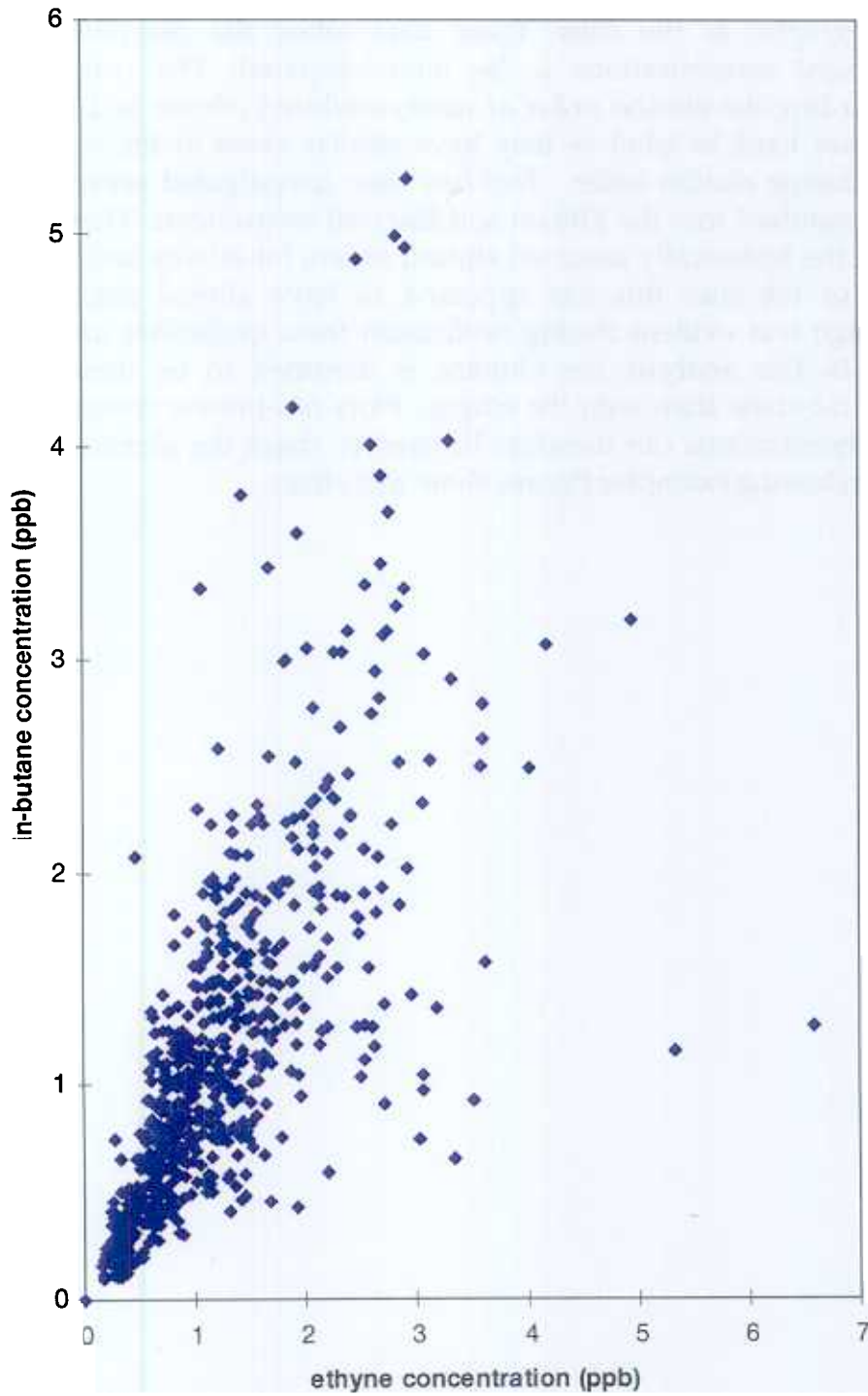
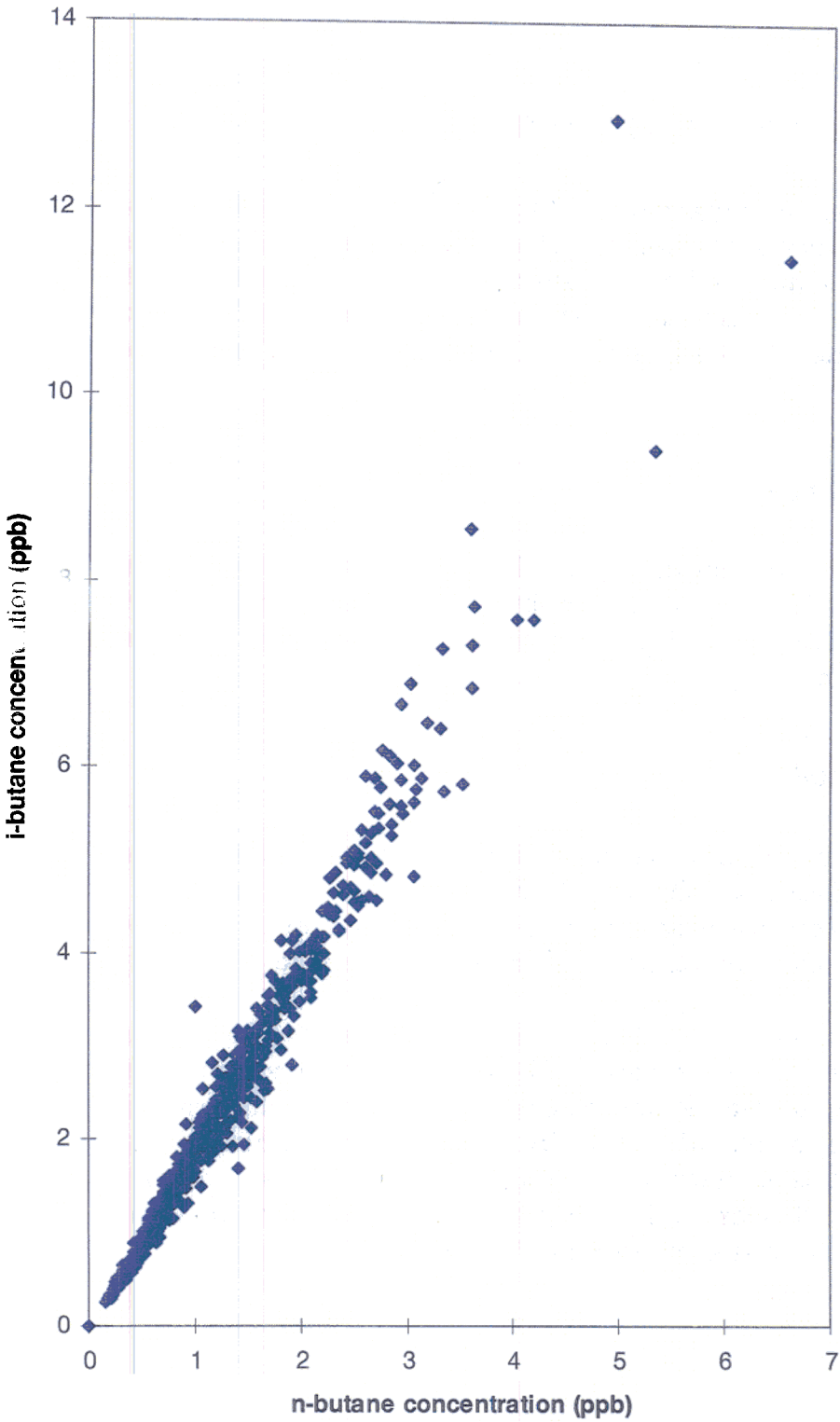


Figure 4 Correlation of i-butane with n-butane



The ambient gas was used to confirm the elution order for ethyne and i-butane at all of the sites. This test agreed with the results of the graphical test used during ratification. In addition a gas mixture containing ethyne only was injected at two sites after the audit visit to confirm the correct identification of ethyne within the ambient audit gas results.

5.2 MARYLEBONE ROAD - AFFILIATED SITE

The audit gases were also injected into the Marylebone road affiliated site. This site, unlike the 12 network sites, uses a Perkin Elmer instrument. This instrument has been set up to run automated calibration runs. The audit gases were injected on 18 March 1998, and the results of an automated calibration on the 17th March were used to provide the site standard results. The results of this audit are still being interpreted.

6. LSO FEEDBACK

An important role of the audits was to allow the LSOs to provide feedback to the CMCU. No major issues were raised by LSOs. Some comments were received regarding the various checklists and forms filled out by LSOs. These comments are under consideration.

7. CONCLUSION

The hydrocarbon monitoring stations are generally in good working order. All equipment is operating satisfactorily. The instigation of Chrompack twice yearly preventative maintenance visits has improved performance. All LSO's are now performing their duties satisfactorily and providing adequate emergency coverage.

Intercomparisons using the three audit cylinders have provided valuable information on network performance. There is good evidence that benzene and 1-3 butadiene are being monitored and reported to the public with an accuracy of better than 10%. Some points identified by these intercomparisons require further investigation and this is under way. As a part of this, max-min thermometers have been installed at all sites to investigate possible temperature effects. Further investigations will be carried out using NPLs own VOC-air system.