

# **AN INTERCOMPARISON BETWEEN AUTOMATIC AND MANUAL METHODS OF MEASURING HYDROGEN CHLORIDE CONCENTRATIONS IN STACK RELEASES**

M J Lewandowski

## **1 ABSTRACT**

The Environment Agency is involved in independent monitoring programmes at a variety of industrial processes where the permits require the measurement of hydrogen chloride (HCl) concentrations in stack releases. The programmes have revealed a number of difficulties associated with the currently used HCl monitoring techniques. Significant differences have been observed between results obtained using manual testing methods and those obtained using continuous emission monitoring systems (CEMs).

Consequently the Agency commissioned a project to compare and assess various measurement techniques under controlled and repeatable laboratory conditions. The work has been carried out by the UK's National Physical Laboratory (NPL). The inter-comparison consisted of a series of tests involving CEMs and Standard Reference Methods (SRMs) using a test chamber developed for the purpose of instrument certification under the Agency's Monitoring Certification Scheme (MCERTS). The facility delivered controlled traceable test gases to the analysers either in across-stack or in an extractive monitoring set-up.

The instrumental methods covered included the gas filter correlation (GFC), differential optical absorption spectroscopy (DOAS), tunable diode laser (TDL), Fourier transform spectroscopy (FTIR)- medium and low resolution, and ion mobility mass spectrometry (IMMS). The two manual methods tested were SRMs as specified by EN1911 and US EPA method 26A.

The tests have demonstrated that in general the instrumental techniques perform well and produce much more repeatable results than SRMs. No major interferent effects were observed across all techniques. The SRMs were not challenged with gaseous chlorides which would have caused much greater discrepancies between the automatic techniques and the manual ones. The performance of SRMs puts a question mark over their use as a principal means of calibration of CEMs especially in view of possible interfering effect of gaseous chlorides.

## 2 LABORATORY TESTING PROGRAMME

### 2.1 Scope of the tests

A series of laboratory tests were carried out to assess the HCl monitoring techniques. The tests performed on the CEMs were:

- Accuracy;
- Accuracy in the presence of interfering species;
- Linearity;
- Linearity in the presence of interfering species;
- Cross sensitivity to interfering species (including water);
- Detection limit;
- Effect of ambient temperature on zero and span readings.

It was not practical to subject the SRMs to the same testing programme as the CEMs, due to the comparatively long time period required for one SRM measurement. The SRMs sampled a series of test gases, containing a range of HCl concentrations, some with interferents present. The test gases were chosen to enable an assessment of :

- Accuracy;
- Linearity;
- Cross Sensitivity

In addition, parallel measurements were made using a subset of the CEMs during the SRM tests to provide a direct comparison of results.

### 2.2 Testing facilities

The test facility was developed to carry out laboratory testing for the Environment Agency's MCERTS scheme for continuous emission monitors and was used to deliver controlled traceable test gases and simulate relevant features of a stack environment. The test facility used for testing the HCl monitoring techniques in the laboratory comprised of a number of components ; a probe chamber, water vapour generator, interferent blender unit, environmental chamber and binary network gas blender.

The probe chamber is a 1 metre long gas-tight chamber mounted in an oven. It was used to simulate the environment that an analyser may be exposed to in a stack. Traceable concentrations of gas mixtures were maintained at controllable temperatures and pressures.

The water vapour generator was used to generate accurate concentrations of water vapour. It mixed known flows of water and dry air and raised the temperature of the mixture to ensure total vaporisation.

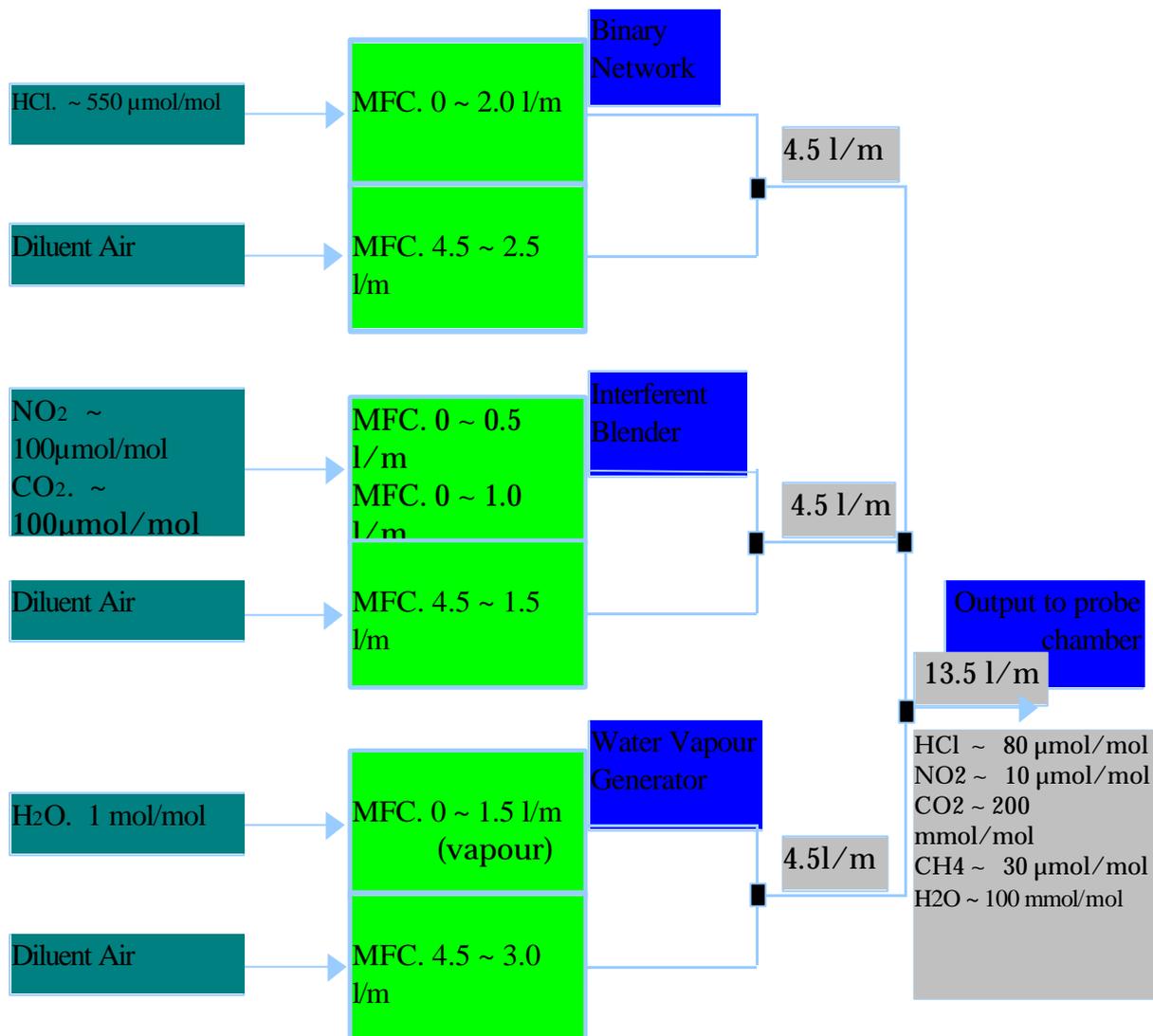
The interferent blender unit is a dynamic dilution system comprising nine mass flow controllers, one of which was used to control the flow of the diluent gas and the remainder controlled the flows of the interferents gases.

The environmental chamber was used to control the ambient environment that cross stack analysers were exposed to. During these tests, the probe chamber, including its oven, was located inside the environmental chamber. Only those components of the CEMs that are mounted on stacks were subjected to the ambient temperature tests.

The binary network is a facility that was used to produce the required, accurate and traceable, gas mixtures. The gas mixtures were produced dynamically using several mass flow controllers (MFC) that were connected in parallel. During the tests the total flow of the gas mixture and the concentration of HCl injected into the probe chamber were kept constant. This was achieved by adjusting the diluent gas flow to the appropriate settings

when each additional interferent was injected, enabling the settings for the HCl, generated using the binary network, to remain stable. The configuration is illustrated in Figure 1.

Figure 1. Schematic diagram of facility generating test gases



### 2.3 Test gases

The accuracy test was carried out using a commercially manufactured HCl standard, which was calibrated by NPL, directly and traceably to UK national standards. This gas had a nominal concentration at 90% of the testing range. The testing range was nominally 0 to 100 µmol/mol of HCl.

The zero gas used was obtained from a compressed air line. This was scrubbed by a catalytic converter to reduce the hydrocarbon content to less than 0.1 µmol/mol, dried to remove water at a dew point of -70°C and filtered to remove particulate matter of diameter greater than 3 micrometres.

The uncertainties of gases used are summarised in Table 1.

Table 1 Uncertainty of Source Test Gases

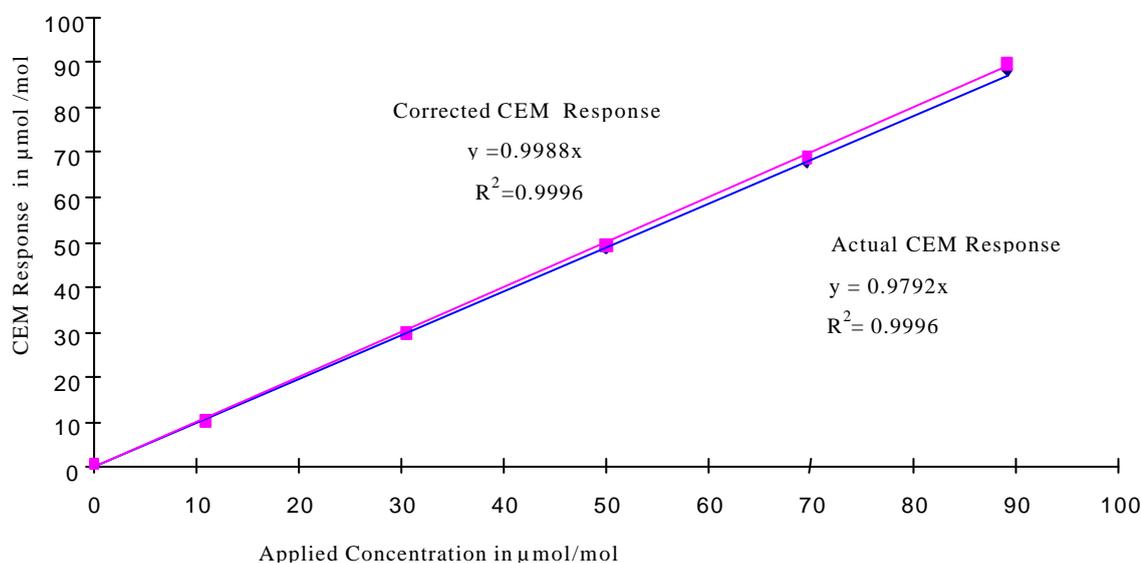
GAS	SUPPLIED CONCENTRATION	NOMINAL	NPL CONCENTRATION AND UNCERTAINTY	MEASURED AND
NO <sub>2</sub> : Bulk	(103 ± 5.15) μmol/mol		-	
CO <sub>2</sub> : Bulk	1 mol/mol		-	
CH <sub>4</sub> : Bulk	(915 ± 18.3) μmol/mol		-	
Water	1 mol/mol		-	
HCl: Bulk 1	532.8 μmol/mol		(587 ± 20) μmol/mol	
Bulk 2	540.2 μmol/mol		(580 ± 20) μmol/mol	
Bulk 3	541.1 μmol/mol		(493 ± 17) μmol/mol	
Bulk 4	542.3 μmol/mol		(621 ± 21) μmol/mol	
Air	1 mol/mol		Water < 500 μmol/mol Particulate < 3 micron	

### 3 TEST RESULTS

#### 3.1 Gas filter correlation (GFC)

The gas filter correlation technique uses a narrow bandpass interference filter to isolate the appropriate region within the infrared spectrum at which the determinand has absorption features. The analyser uses two hermetically sealed gas filled cuvettes on a rotating chopper to modulate an infrared beam that has been passed through a cell containing the sample gas. Normally one of the cuvettes is filled with nitrogen and the other with the determinand gas (in this case HCl). The infrared beam then falls onto a detector. The detector receives two alternating signals: one, the 'sample' signal, is unattenuated through the nitrogen cuvettes, the other, the 'reference' signal, is attenuated by the specific fine absorption bands produced by the HCl cuvette. When the analyser is exposed to the sample gas the 'sample' signal is attenuated due to the presence of any HCl in the sample gas removed. The analysis function obtained during the tests is shown in Figure 2.

Figure 2 GFC response to HCl corrected for accuracy-test result, interferences present

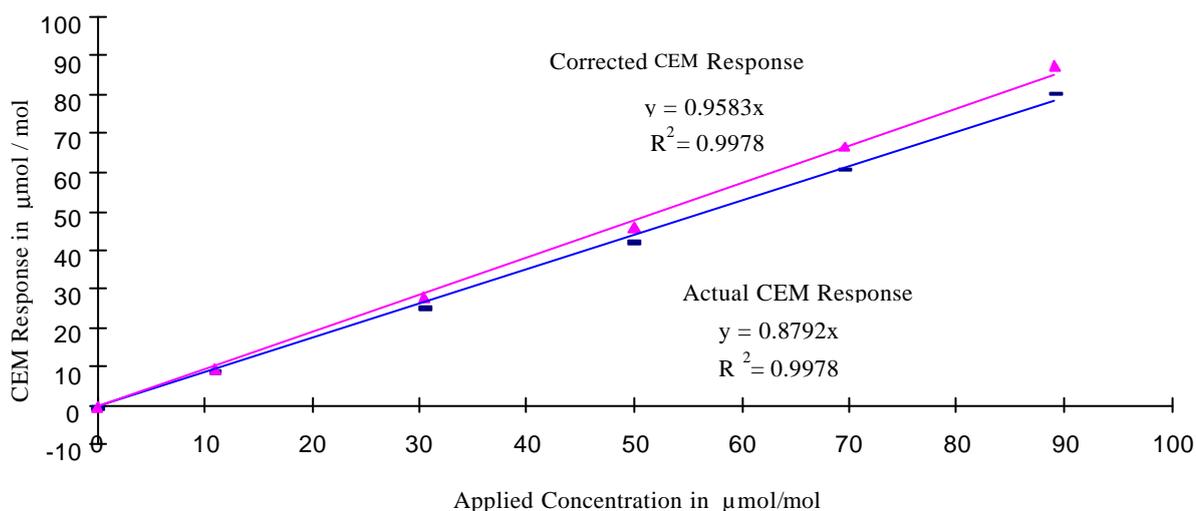


### 3.2 Differential optical absorption spectroscopy (DOAS)

Differential Optical Absorption Spectroscopy is used to measure the concentration of gases by determining the gradient of an absorption peak. This is achieved by measuring the difference between the absorbance at a wavelength where the sample gas has produced a distinctive absorption peak, and at one or more wavelengths on either side of the peak.

The technique uses white light produced from a continuous light source, (in this case a high pressure Xe lamp), to form a parallel beam using a focusing mirror. The parallel light passes through the sample cell, then reflects off a mirror which focuses the light into the entrance of a monochromator. The grating of the monochromator disperses the light so that the spectrum is projected on to a mask. This allows the segments of the dispersed spectrum to fall on to a rotating wheel, with the central wavelength set by the monochromator wavelength setting. The rotating wheel contains a number of narrow slits, which scan the portion of the spectrum dispersed across the monochromator exit slit and pass it to a detector. The signal, detected using a photomultiplier, is measured at numerous locations across the exit aperture, and these signals are stored in different channels and are analysed to determine the HCl concentration. The analysis function obtained during the tests is shown in Figure 3.

Figure 3 DOAS response to HCl corrected for accuracy-test result, interferences present



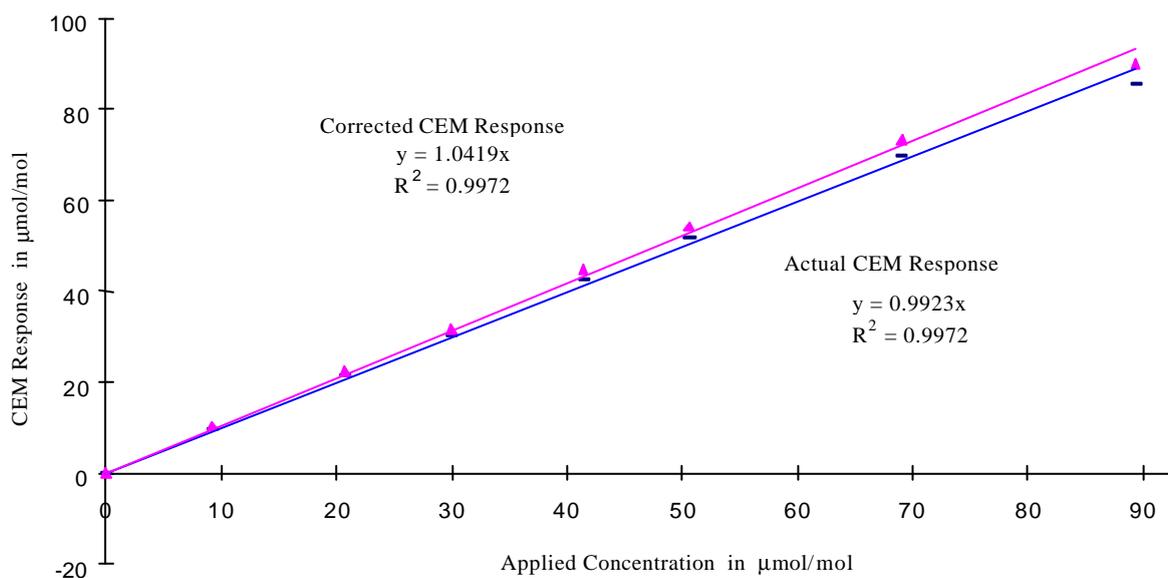
The data processing of the DOAS analyser incorporated a correction for the presence of water. Therefore, the concentration of HCl should not have been affected by water vapour. However, when the analyser was exposed to 80 μmol/mol of HCl with 10pph of water vapour, the observed concentration of HCl decreased by approximately 10 μmol/mol. A plausible explanation for this effect is related to the calibration of the water channel in the analyser. When the analyser was exposed to 10pph of water vapour it measured the concentration of the water vapour to be between 15-20pph. This suggests that the calibration of the water channel in the analyser may have drifted, decreasing the concentration of HCl by approximately 10 μmol/mol in the presence of water. This is not an inherent fault with the DOAS technique, but it does highlight potential problems with analysers which correct for intereferent effects.

### 3.3 Fourier transform infrared spectroscopy (low resolution FTIR) - automated data analysis

An FTIR spectrometer consists of an infrared source that emits a broad band of wavelengths of infrared radiation. The infrared radiation is passed through an interferometer which modulates the signal. The interferometer performs an optical inverse fourier transform on the signal, then passes the modulated infrared beam through the gas sample. The intensity of the infrared beam is measured by a detector, the signal is digitalised, and Fourier transformed by a computer to obtain the infrared spectrum of the sample gas.

The low resolution FTIR analyser extracted the gas sample through a 5 metre long heated line. The calibration was carried out by the manufacturer. The analyser gave a digital output that displayed its readings in  $\mu\text{mol/mol}$ . The resolution of the analyser used was 8 wavenumbers. ( A wavenumber is a spectroscopic unit. It is an inverse wavelength, one wavenumber is equal to  $1\text{cm}^{-1}$ ).

Figure 4. Low resolution FTIR response to HCl corrected for accuracy-test result, interferents present

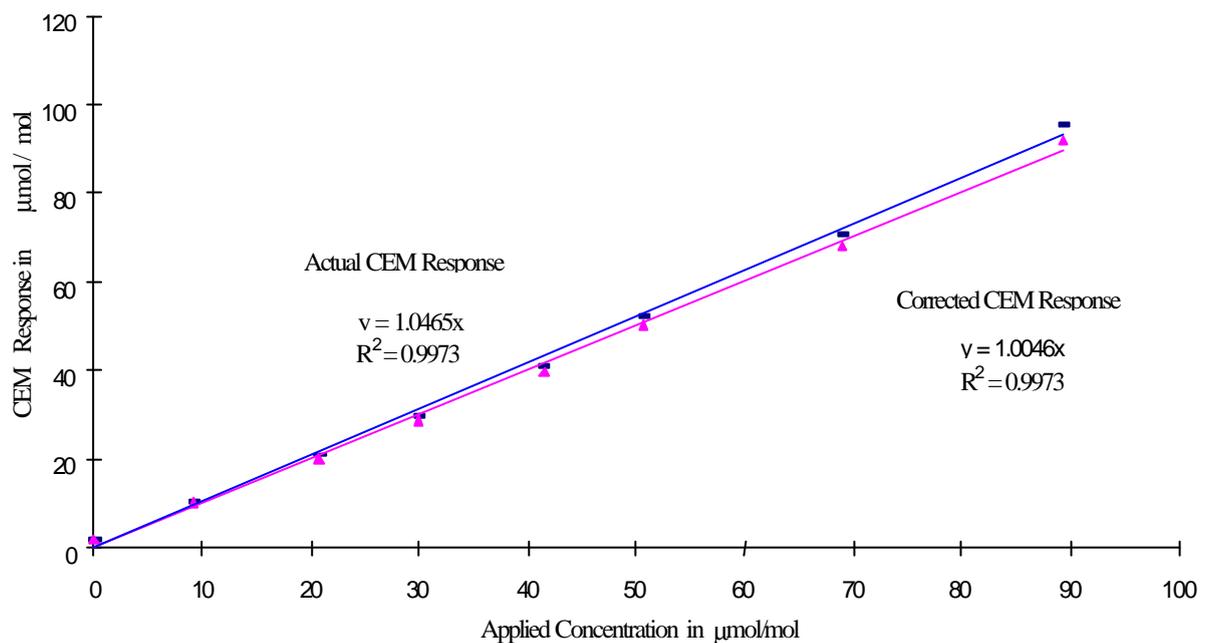


### 3.4 Fourier transform infrared spectroscopy ( medium resolution FTIR) automated data analysis

The medium resolution FTIR system used the same technique as the low resolution system, but with a higher spectroscopic resolution (1 wavenumber).

The medium resolution FTIR analyser extracted the gas sample through a heated line that was 5 metres long. The calibration used was carried out by the manufacturers. The analyser gave a digital output that displayed readings in  $\mu\text{mol}/\text{mol}$ . The analysis function obtained during the tests is shown in Figure 5.

Figure 5. Medium resolution FTIR response to HCl corrected for accuracy-test result, interferences present.



The medium resolution FTIR analyser initially had a problem related to the sampling system. This became apparent when the analyser was exposed to 80  $\mu\text{mol}/\text{mol}$  of HCl in the presence of 10pph of water vapour, The concentration of HCl decreased to 38.1  $\mu\text{mol}/\text{mol}$  in the presence of water. The problem was identified as the sample line particulate filter. The purpose of the filter was to eliminate any particulate matter with a diameter greater than 3 microns. However, the filter appeared to remove a significant proportion of HCl in the presence of water vapour. The heated line was removed from the inlet to the sampling system, and attached directly to the sampling cell. When the test was repeated, the concentration of HCl increased to 83.9  $\mu\text{mol}/\text{mol}$  in the presence of water. This higher value can be explained by a spectral broadening effect that many of the optical analysers appeared to experience.

In order to resolve any doubts relating to the data processing of the automated FTIR analysers, the raw data obtained from the Medium Resolution FTIR spectra were manually re-processed, and the results noted, enabling a direct comparison between the automated and manual results.

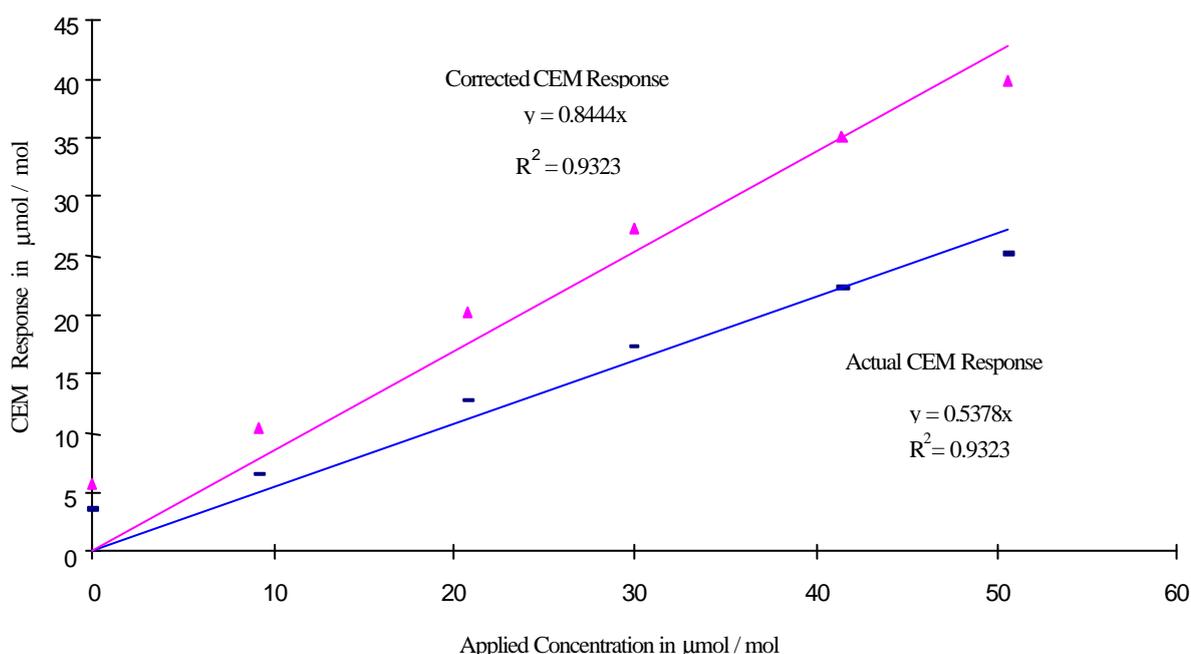
### 3.5 Ion mobility mass spectroscopy (IMS)

Ion Mobility Mass Spectrometry, (IMS), operates in a similar way to an atmospheric pressure time of flight mass spectrometer. All mass spectrometers consist of: an ion source which ionises the sample molecule, a mass analyser that differentiates the ions according to their mass-to-charge ratio, and finally a detector which measures the ion beam current.

In the analyser tested, an IMS cell was used to detect the sample gas. The sample was indirectly ionised using a  $\text{Ni}_{63}$  ring, a beta ionisation source, within the sample cell. The resultant ion clusters were separated in the presence of an electrical field to generate spectra which were measured on the detector. The concentration of the sample gas could then be determined.

The IMS analyser extracted the gas sample through a heated line that was 5 metres long. The calibration was carried out by the manufacturer. The analysis function obtained during the tests is shown in Figure 6.

Figure 6 Ion mobility Spectroscopy response to HCl corrected for accuracy test results, interferences present.



A number of problems were encountered which affected the performance of the IMS analyser in the laboratory environment. However, these problems would not necessarily be relevant if the analyser was operated in a typical industrial environment, where it would normally be operated with a dilution facility. In order to operate the analyser with the test facility it was necessary to set it up in an atypical configuration.

The problems encountered were:

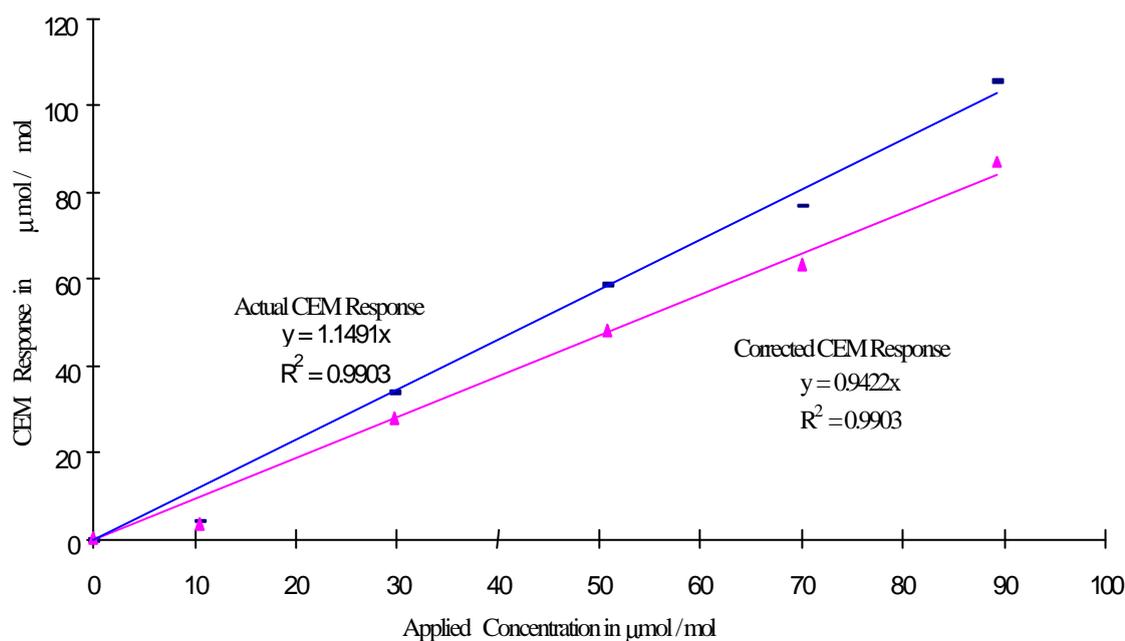
- the analyser signal went off scale (below zero) when exposed to zero gas;
- a lack of insulation around the internal cell;
- significant analyser noise;
- pressure effects on the flow rate.

### 3.6 Tunable diode laser (TDL)

Tunable diode laser spectroscopy is used to measure the concentration of gases via an optical method using the principle of selective infrared absorption by the gas molecules. The TDL operates in the near infrared spectral range (NIR) producing narrow linewidth light, that is tunable over a small wavelength range. The analyser is capable of operating at a single frequency, which can be tuned by temperature and/or current. Several different modulation techniques can be adopted to increase the signal to noise ratio. This involves modulating the output of the laser by modulating the current, and thus temperature of the diode, to measure the concentration of the sample gas. Due to the wide range of gases that have a single absorption line in the NIR, the TDL analyser can select multiple absorption lines at different frequencies. The lines produced are generally the overtone lines from the fundamental absorption lines due to the rotational and vibration modes of the molecules.

The basic technique behind the TDL involves scanning the laser over the absorption line. To improve the detection sensitivity the technique applies a modulation of the laser frequency. The modulation frequency used is significantly less than the width of the absorption line, so that the formation of the second harmonic component of the signal produced can be used to quantify the concentration of the sample gas. The analysis function obtained during the tests is shown in Figure 7.

Figure 7. TDL response to HCl corrected for accuracy-test result, interferences present



A number of problems were experienced with the TDL analyser:

- a decrease in transmission due to ambient vibrations;
- spectral broadening of the sample gas absorption line when exposed to interferences;
- miss-identification of HCl when exposed to methane;
- loss of sensitivity in the presence of water vapour.

In addition the technique, in common with other purely spectroscopic techniques, was incapable of monitoring molecules bound in complex compounds.

The TDL analyser was found to be very sensitive to the alignment of the optical beams, and this caused the instrument to be sensitive to vibration. If the analyser were to be subjected to typical vibrations on a stack it is possible the transmission, and hence the sensitivity, might be affected. This is a potential problem with cross stack instruments in general.

The spectral broadening of the absorption line caused the analyser to read the concentration of the sample gas incorrectly when simultaneously exposed to interferents. The broadening was due to absorption lines from the interferent gases overlapping with the HCl absorption lines. This gave an apparent decrease in the HCl concentration. This was caused by the base of the HCl absorption peak being broadened by the absorption peak of the interferent gas and in turn causing the baseline reading to be too high, resulting in a reduced HCl reading. This effect is a feature of the choice of spectral region used to detect HCl and in principle is not an inherent problem with the technique. However, this does highlight an area of potential concern in any spectroscopic technique.

When the analyser was exposed to methane as one of the individual interferents a further problem emerged. The analyser 'locked' on to the methane absorption feature and identified this as HCl. This would appear to be a feature of the data processing software within the analyser. In the presence of HCl the analyser had correctly identified the HCl peak, however when the HCl was removed and replaced with methane this was incorrectly identified as HCl. Due to both the HCl and methane absorption peaks having relatively close wavelengths the analyser detected the methane peak as an HCl peak. A further complication was that when the analyser was subsequently exposed to HCl it did not respond, which implies that the lock to the incorrect, methane, wavelength had been maintained.

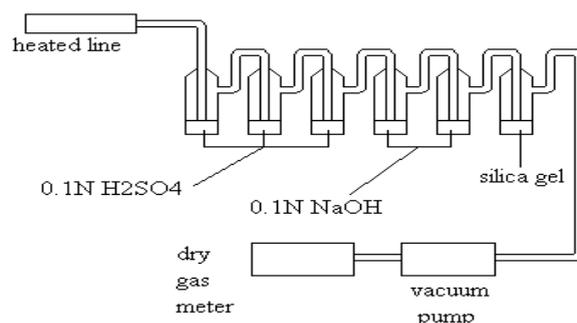
The analyser also exhibited an apparent loss in sensitivity in the presence of water vapour. A possible explanation for this is hydrogen bonding. The water molecules that are injected into the probe chamber tend to form a very strong dipole-dipole attraction to the HCl molecules, known as a hydrogen bond. This means the hydrogen atom serves as a bridge between two electro-negative atoms, holding one by a covalent bond and the other by an electrostatic force. When 10pph of water vapour is injected into the probe chamber with 80  $\mu\text{mol/mol}$  of HCl, the water molecules start to form hydrogen bonds with the hydrogen atoms in HCl. The HCl atoms in a hydrogen bond will have broader absorption spectra than free atoms. Therefore, the analyser will detect a broader spectral band than that seen under calibration conditions, resulting in a decrease in the sensitivity of the analyser when exposed to water.

### 3.7 Manual sampling method EPA 26A.

The manual testing methods measure the emissions of hydrogen halides and halogens from a stationary source. The basic principle involves extracting the sample gas isokinetically from the source then passing it through a heated line and a filter, into an absorbing solution that collects the gaseous hydrogen halides and halogens. The filter is used to collect particulate matter such as halide salts. The hydrogen halides form ions in the solution. The manual testing used a set of 'mini' impingers to collect the HCl. Two separate techniques were compared: method 26A and EN1911-1.

The methods were each used to sample the test gas from the probe cell over 12 hourly sampling periods. The concentration of the test gas was kept constant for each hourly sample. Some samples had water vapour present, the rest used dry gas. The sampling system used to perform the manual method 26A is shown in Figure 8.

Figure 8 Sampling System for ManualMethod 26A.



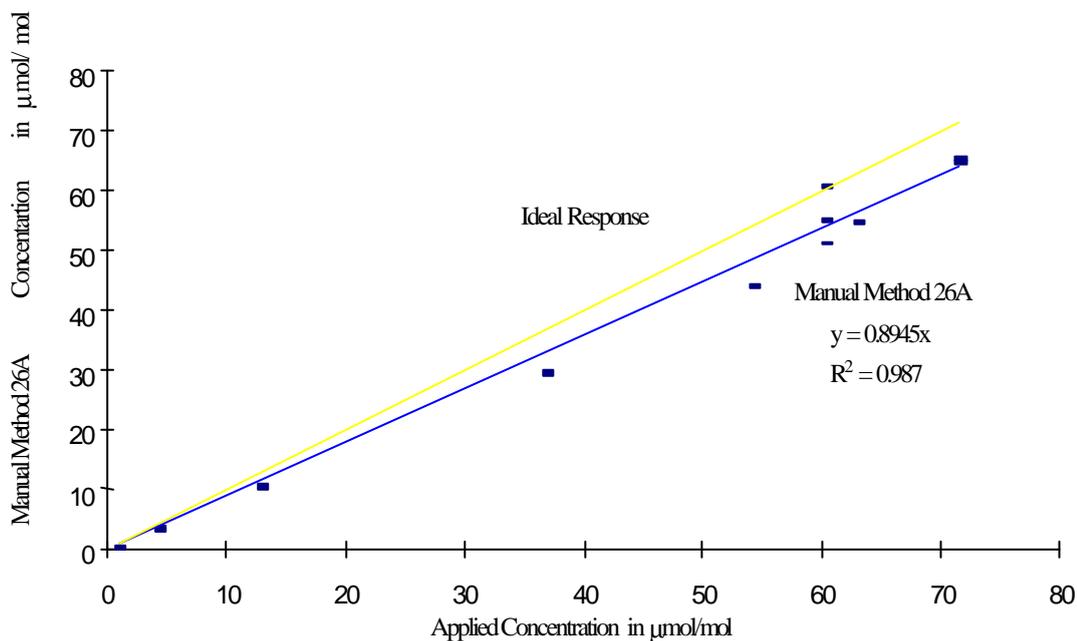
The results obtained with manual extractive method 26A are shown in table 2.

Table 2

Applied Sample Gas	Applied Concentration $\mu\text{mol/mol}$	Result $\mu\text{mol/mol}$
HCl	2.2	0.4
HCl	4.4	3.6
HCl	54.4	43.9
HCl	60.4	54.1
HCl	13.0	10.6
HCl	71.6	64.8
<hr/>		
HCl + NO <sub>2</sub>	4.4 + 9.9	3.3
HCl	60.4	50.8
HCl + H <sub>2</sub> O	60.4 + 11.1 pph	53.5 + 12.2 pph
HCl	63.1	54.7
HCl + H <sub>2</sub> O	71.6 + 13.2 pph	56.1 + 14.6 pph
HCl	37.0	29.3
<hr/>		

The graph shown in Figure 9 illustrates the CEM response of the manual testing method 26A in comparison to the applied concentrations.

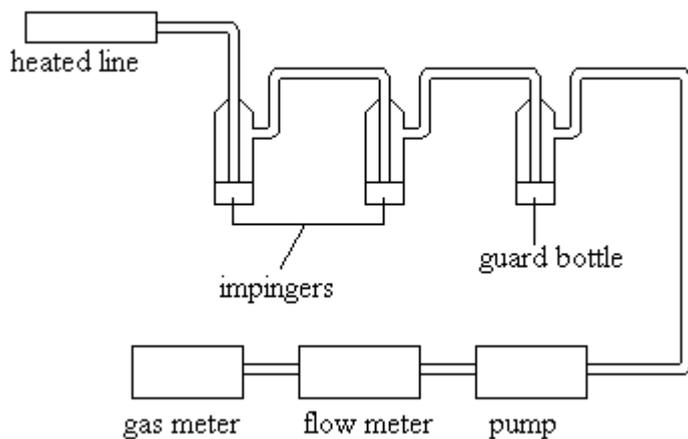
Figure 9. Response of manual Method EPA 26A to HCl



### 3.8 Manual sampling method EN 1911

The sampling system used to perform the manual method EN 1911 is shown in Figure 10.

Figure 10 Sampling System for Manual Method EN 1911-1



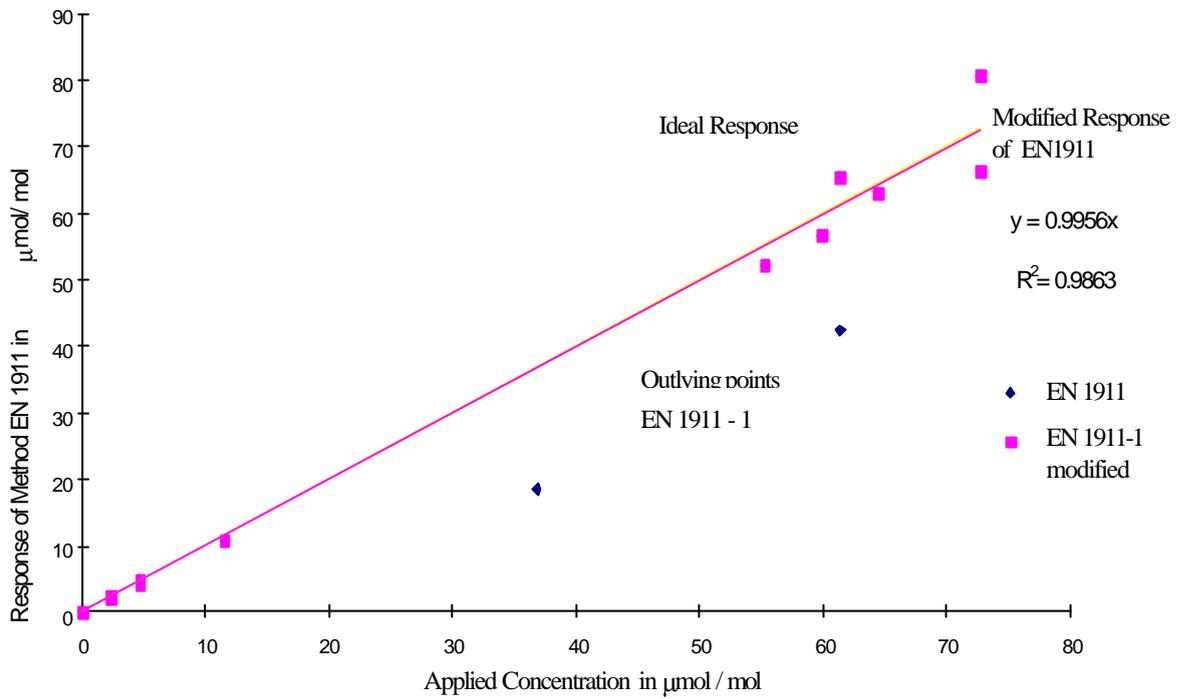
The results obtained for the manual testing method EN1911 are summarised in table 3.

Table 3

Applied sample gas	Applied concentration (µmol/mol)	Result (µmol/mol)
HCl	2.3	2.3
HCl	4.6	4.2
HCl	55.2	52.2
HCl	59.8	56.6
HCl	11.5	10.7
HCl	72.8	66.4
HCl + NO <sub>2</sub>	4.6 + 9.9	4.8
HCl	61.4	65.4
HCl + H <sub>2</sub> O	61.4 + 11.1 pph	47.7
HCl	64.4	63.0
HCl + H <sub>2</sub> O	72.8 + 13.2 pph	92.8
HCl	36.8	18.4

The graph shown in Figure 11 illustrates the CEM response of the manual testing method EN 1911-1 in comparison to the applied concentrations.

Figure 11 Response of manual method EN 1911 to HCl



#### 4. A SUMMARY OF THE HYDROGEN CHLORIDE INTERCOMPARISON RESULTS

Table 4 Summary of the results obtained for automatic analysers

Performance Characteristic	DOAS	TDL	GFC	Low Res. FTIR	High Res. FTIR Automated Data	High Res. FTIR Manual Data	IMS
CEM Range ( $\mu\text{mol/mol}$ )	-10-100	-10 - 100	0 - 100	0 - 100	0 - 100	0 - 100	0 - 70.69
<i>Response Time (sec)</i>	245	32	216	180	180	180	180
<i>Accuracy of Response ( % of applied concentration)</i>	7.5	(6.0) <sup>1</sup> 13.1	2.7	-4.6	-4.4	-	-13.9
<i>Accuracy of Response in the Presence of a Mixture Interferents (% of applied concentration)</i>	-9.4	(18.0) <sup>1</sup> 5.3	-2.0	2.2	4.4	-	-57.2
<i>Linearity Error (% of full scale)</i>	0.2	-0.3	-0.2	-2.4	-1.1	-	0.4
<i>Linearity Error in the Presence of a Mixture of Interferents (% of full scale)</i>	-0.2	-0.7	0.1	2.3	2.5	-	-0.3

<i>Cross Sensitivity Tests</i>							
<i>Applied Conc. of HCl for span reading (mmol/mol)</i>	80.4	80.4	80.4	80.6	80.6	80.6	50.6
<i>( The following sensitivity results are presented as % of full scale)</i>							
NO <sub>2</sub> :- The effect on zero	-0.1	0.2	-1.1	0.02	1.6	-	1.8
NO <sub>2</sub> :- The effect on span	0.3	1.9	-0.5	0.2	1.3	-	-11.6
CH <sub>4</sub> :- The effect on zero	-0.5	0.1	-1.0	0.3	2.3	-	-0.7
CH <sub>4</sub> :- The effect on span	-1.1	2.1	-0.1	0.8	1.6	-	0.3
CO <sub>2</sub> :- The effect on zero	0.7	0.7	-1.2	0.3	2.1	-	-0.4
CO <sub>2</sub> :- The effect on span	-0.9	-0.4	-1.0	3.3	4.3	-	3.2
H <sub>2</sub> O:- The effect on zero	-0.3	0.2	0.5	1.1	2.5	1.8	-1.0
H <sub>2</sub> O:- The effect on span	-10.0	-8.4	-5.1	7.3	-31.2	-30.6	-3.7
H <sub>2</sub> O:- The effect on zero	-	-	-	-	0.8	0.6	-
H <sub>2</sub> O:- The effect on span	-	-	-	-	7.8	7.5	-
(without sampling system)							
Sum of single component interferents <sup>2</sup> The effect on zero	-0.2	1.2	-2.8	1.7	8.5	-	-0.3
Sum of single component interferents <sup>2</sup> The effect on span	11.7	-4.8	-6.7	11.6	-24.0	-	-11.8
Cocktail:- The effect on zero	-0.7	0.3	1.6	3.4	2.1	-	1.2
Cocktail:- The effect on the span	-8.0	-6.0	-5.2	7.7	-27.6	-	-27.0

## 5 CONCLUSIONS

The results of the tests show that in general the CEM techniques performed well, and gave more representative results than the manual techniques. Some of the problems which occurred with the CEMs were due to analyser design, while others were due to faults with the particular equipment being tested. While these are not indicative of problems with the techniques themselves, they do highlight the importance of good design, reliable manufacture and adequate testing and calibration of installed equipment. A number of the faults observed would not have been evident had they occurred in equipment installed on a stack. The Monitoring Certification Scheme (MCERTS) introduced in the UK by the Agency is aimed at demonstration of fitness for purpose of equipment and helps to avoid the kind of problems that came to light in the present study.

The various problems observed have also highlighted a number of issues with spectroscopic techniques in general. The potential for overlapping absorption bands means that these techniques may be particularly sensitive to interferents. In addition, reference and zero spectral measurements must be free from interferent absorption peaks. The performance of systems using such techniques will depend upon the correct choice of spectral region by the manufacturer. Accurate calibration of such analysers is also fundamental, and care should be taken to ensure that no assumption is made by the manufacturer as to the matrix within the gas (for example presence of water vapour).

CEMs should also be used within the range of conditions specified by the manufacturer, and it is important that they are installed and configured correctly. The effect of operating an analyser outside its normal operating conditions can be seen in the results obtained from the IMS system. In this case operating the analyser in a configuration which delivered a concentration of water vapour which was above that recommended for the analyser caused significant errors.

All analysers had response times of less than 4 minutes, which for most stack applications is well within requirements.

The results of the accuracy test were within 15 % of measured value for all analysers. The IMS had an error of 13.5%, which may have been due to the configuration in which it was operated, as discussed above. The TDL initially gave a response which was 6% in error. After recalibration by the manufacturer this changed to 13%, but the response to water vapour changed after this recalibration, and it appears the analyser was recalibrated with wet gases. The accuracy errors were in general due to the calibration artefacts used by the manufacturers. The results from the tests have been quoted as 'corrected results' when they have been scaled to take account of the accuracy test results. This allowed for better comparison between different techniques. No major systematic interferent effects were observed across all the techniques. Some analysers were susceptible to water vapour interference. This manifested itself as a quenching effect in all techniques apart from the low resolution FTIR which gave a positive response to water vapour. It is worth noting that the TDL analyser initially gave larger positive response to the accuracy test in the presence of interferents than it did to HCl alone. However, after the analyser had been returned to the manufacturer for recalibration its response to HCl alone was higher than its response to HCl in the presence of interferents. Examining the analyser's response to individual interferents it is clear that this was mainly due to a relatively high sensitivity to water vapour.

The manual methods are known to be sensitive to total chlorides rather than HCl specifically. This response, which is an inherent part of the methods, was not challenged in these tests. It should be noted however that under field conditions, chloride ions might well be present in a number of forms other than HCl.

In general, the manual methods performed less consistently than the CEMs. The linearity of the manual methods was acceptable but not as good as most of the CEMs. The manual methods showed no consistent systematic effect due to the presence of water vapour or NO<sub>2</sub>. Two results from EN 1911 had to be treated as outliers, as shown in Figure 11.

All the tests were performed under laboratory conditions. The techniques were presented with test gases which had a more uniform matrix than would often be found under real conditions. The overall performance of the techniques was encouraging. The largest source of error in most cases was due to the calibration of the system. The tests of manual methods have shown a baseline for the performance of these techniques under close to ideal

conditions. They have shown that under these conditions the techniques are capable of producing reasonably consistent results, and inconsistencies of the magnitude observed under field conditions have not been seen.

## BIOGRAPHICAL DETAILS : MACIEK LEWANDOWSKI

Environment Agency  
National Compliance Assessment Service  
Lancaster, LA1 4XQ, UK

Phone: 01524 581931 Fax: 01524 842709 E-mail: [maciek.lewandowski@environment-agency.gov.uk](mailto:maciek.lewandowski@environment-agency.gov.uk)

Maciek Lewandowski is a Technical Manager in the National Compliance Assessment Service of the Environment Agency. His responsibilities include technical guidance on monitoring of stack emissions and ambient air quality. His main area of work is the implementation of the MCERTS scheme for ambient air quality monitors. He participates in the work of three working groups of CEN TC 264. Before joining the Agency he worked in the field of environmental consultancy dealing with environmental impact assessments, stack monitoring exercises, operation of ambient air quality monitoring networks and development of calibration systems for automatic analysers.