NPL REPORT DQL-AS 004

Measurements Performed at a Fibreglass Manufacturing Plant using FTIR Spectroscopy and Wet Reference Methods

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Report

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Executive Summary.

On-line, real-time quantitative measurements of HCl, HF, SO_2, H_2O, CO, CO_2, NO, NO_2 and NH_3 by FTIR spectroscopy have been successfully demonstrated at a fibreglass manufacturing plant. It has also been shown that employment of such an instrument on-site could save ~£27k p.a. in terms of monitoring costs. Trend data for all species is shown detailing high concentrations of HF, SO_2, H_2O and CO_2 along with lower concentrations of the remaining species.

An intercomparison against wet reference methods (namely USEPA 26 and a measurement contractors "in-house" method) used for determining HCl and HF concentrations is described. The concentrations reported by the FTIR (measured spectra were analysed using the on-line commercial software package) agreed well with both the USEPA and in-house methods. Although, the difference between the latter was slightly greater. It was proposed that this was due to the fact that this method could not discriminate between HCl and Cl_2. Consequently, any Cl_2 present (small amounts were detected by the USEPA method) could appear as HCl. To substantiate the conclusions from the HCl comparison the degree of validity of the commercial on-line analysis package employed with the FTIR instrument was determined *via.* modelling. An NPL developed least squares fitting routine was used to fit an HCl model to the raw measured spectra, consequently, determining a fitted concentration. There was good agreement between the concentration of HCl fitted by the model and that determined by the on-line analysis software.

In contrast, there was a poor agreement between the FTIR and the two wet reference methods for HF quantification. With regard to the USEPA method the results were variable, whereas for the in-house method there was surprisingly no HF detected.

The field trial has demonstrated the applicability of FTIR for performing on-line, real-time measurements of multiple species. Measurements of HF are not only important to the fibreglass manufacturing community but are also necessary in the brick works industry. Furthermore, the applicability of the spectrometric measurements demonstrated in this field trial stretches even wider since many of the gasses encountered (*e.g.* HCl, NO_x) are also common to many regulated industrial process emissions.

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Approved on behalf of the Managing Director, NPL
by Stuart Windsor, Business Leader, Quality of Life Division

Case Study Rationale.

The case study described in this report was performed at a fibreglass manufacturing plant and was selected for three main reasons.

- It was estimated that successful measurement of HCl, HF and other typical combustion gases would save the plant ~ £27k per annum, hence demonstrating the validity of FTIR for this measurement was important.
- It would provide an opportunity to perform an inter-comparison with wet chemical reference methods used for measuring HCl and HF (validity of measurements was ranked very highly by the companies surveyed).
- The solution would be generic in terms of it's applicability, not only to other fibreglass manufacturers in the UK, but also to a range of other industries including aluminium smelting plants and brick works, that also need to monitor acidic species such as HF.

Theory and Description of Measurements.

Three measurement protocols were employed for the study.

- PC interfaced Bomem 9100 FTIR analyser (a non-destructive technique).
- USEPA Method 26.
- Measurement contractors' "in-house" method based on USEPA Method 26.

Measurements are presented for the FTIR used in isolation and also used as part of an intercomparison against the two wet reference methods. For the intercomparison NPL purchased the services of the measurement contractor usually employed by the plant. This was to ensure that the in-house method was performed exactly as designed by the contractor. The FTIR instrumentation was operated at all times by only the NPL team.

The gas cell on the FTIR analyser has a volume of 5 L and it is recommended that sample gas is pumped through at 2 $Lmin^{-1}$, whilst a pressure of 1 atm is maintained. The gas cell is heated to 173 °C which yields the coupled advantages of not only eradicating any problems caused by condensation of steam (if liquid water is allowed to form it could dissolve out of the gas stream water soluble species such as HCl yielding artificially low readings) but also of allowing an accurate determination of steam concentration. The IR beam (Fourier wave) is reflected several times off mirrors either end of the cell resulting in a pathlength of 6.4 m. The resultant signal is then received at a DTGS (deuterated triglycine sulphate) detector and a Fourier transformation is applied by the interfaced PC, yielding a spectrum of transmission as a function of wavenumber. The automated real-time commercial analysis package then determines concentrations for the species present by using a regression matrix trained using chemometric algorithms. The sampling frequency is set to 60 s for this application, although this is adjustable. Further details of this instrument can be found at the Bomem website (www.abb.com/analytical).

To summarise the wet reference methods; the USEPA method (for greater detail see the EPA website www.epa.gov/ttn/emc/) employs a train of six impingers. The first is empty and is used as a catch pot, the second and third are filled with an aqueous sulfuric acid solution

which dissolves hydrogen halides (HCl, HF and HBr). The fourth and fifth impingers contain an aqueous sodium hydroxide solution to dissolve halogens (Cl_2 and Br_2) (it should be noted that HBr and Br_2 were not emission species at this plant). The sixth impinger contains silica gel to protect the pump. The contractor was asked to perform this method firstly because it is a recognised procedure, and secondly because the chloride found in the H_2SO_4 pots could be directly compared to the HCl reading on the FTIR instrument. The in-house method employs eight impingers (using Teflon rather than glass), the first seven are filled with aqueous hydrogen peroxide and the last with silica gel. The H_2O_2 will dissolve both hydrogen halides and halogens together, hence from the chloride found in the solution it is impossible to tell if this is due to HCl or Cl_2 in the sample gas. Consequently, since the FTIR does not measure Cl_2 (due to a spectroscopic selection rule) a direct comparison is more difficult. The contractor was asked to perform their in-house method since this was the method they had employed on previous measurement campaigns. In all cases the samples collected were sent for analysis by ion chromatography at a UKAS accredited lab.

Prior to the inter-comparison the FTIR was operated in isolation (as Fig.1 except without impinger train) to demonstrate that the technique could record real-time concentrations of all the species of interest.

For the intercomparison measurements the FTIR was coupled in series to either the USEPA or in-house impinger train (Fig. 1). These two experiments were alternated, i.e. a one-hour comparison against the USEPA method would be performed followed by a one-hour comparison to the in-house method. This cycle was repeated four times over three days. As a QA check samples from both techniques from the last measurement cycle were sent to an additional UKAS accredited lab for parallel analysis by ion chromatography.

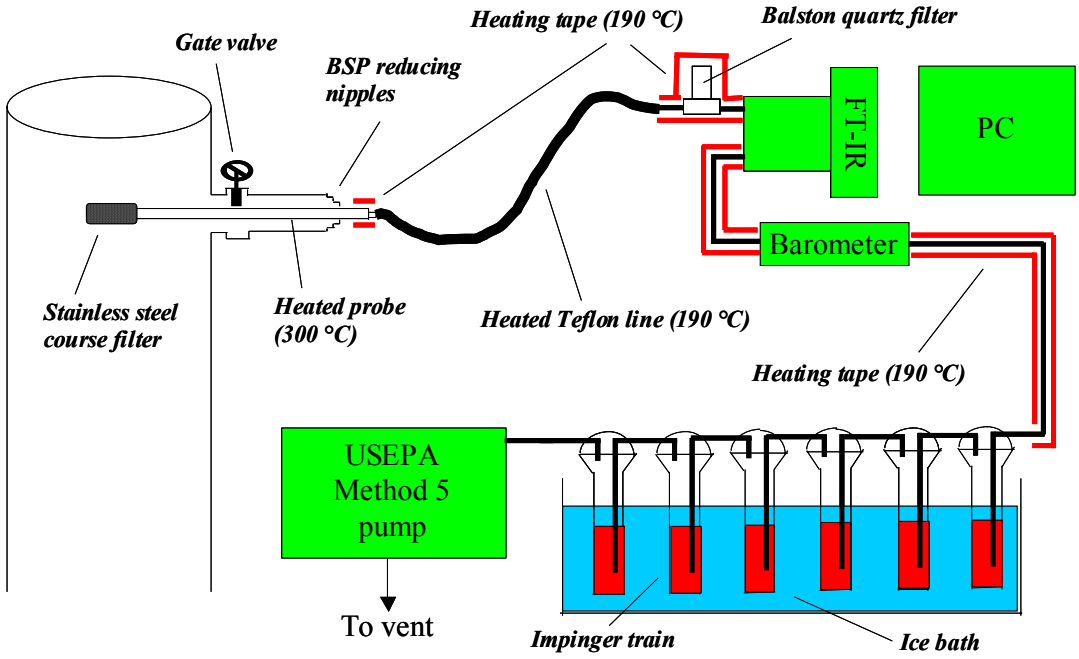

Fig.1 *Schematic of apparatus employed for FTIR / wet reference methods inter-comparison.*

FTIR Measurements.

Performing FTIR measurements (in the absence of an impinger train) identified the key species present and their concentrations in real-time (Figs. 2 & 3).

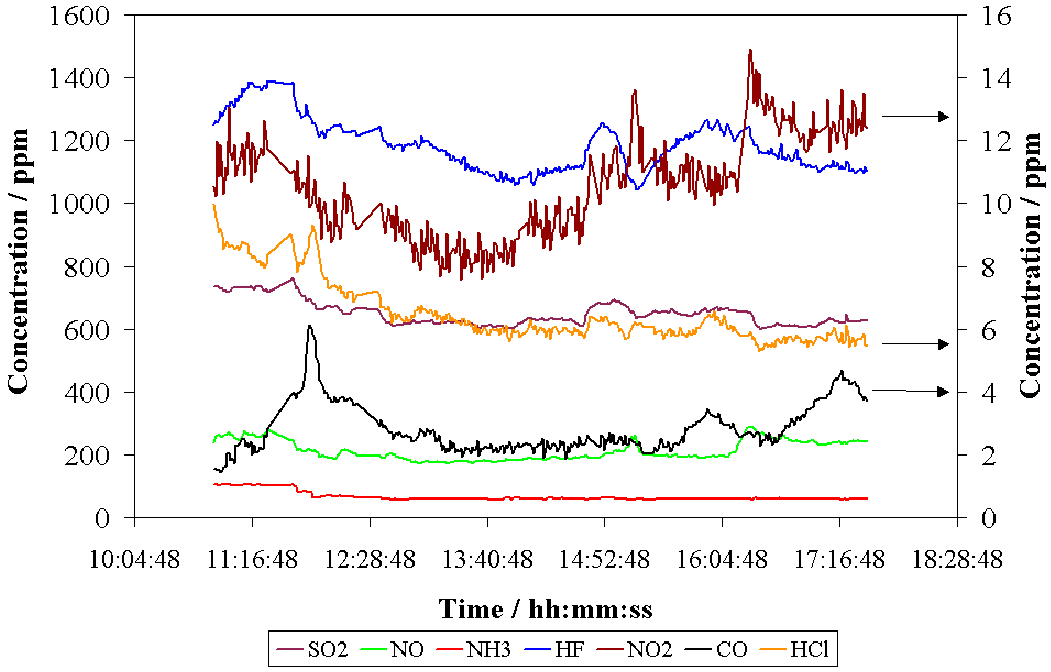

Fig. 2 *Concentration profiles as a function of time on Wednesday 10/07/02. White cell set at a flow rate of 2 Lmin^{-1}, 173 °C and 1 atm.*

There are two points of note from this set of data, namely, the high concentration of HF and the fact that NH_3 was measured. Whilst noteworthy, the former is within expected parameters and correlates with levels commonly reported by contractors performing wet chemical monitoring techniques on the stack. The latter was interesting given that the stack is above a furnace operating at 1600 °C, *i.e.* a net oxidising environment whereas NH_3 is a reduction product. These measurements demonstrate the capability of on-line FTIR to provide real-time measurements of multiple species.

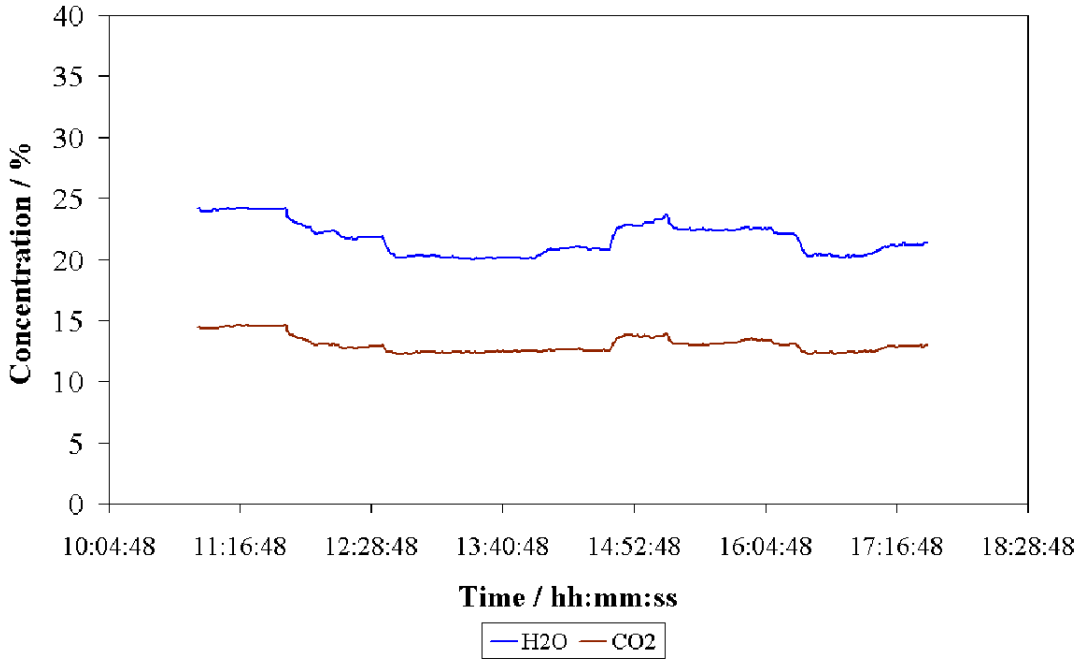

Fig. 3 *H_2O and CO_2 concentrations as a function of time on Wednesday 07/10/02. White cell conditions as detailed in Fig. 2.*

Comparing FTIR and Wet Reference Method Measurements of HCl.

There was a very close correlation between HCl measured on the FTIR and Cl^- (it is assumed this predominately originates from HCl) measured by USEPA method 26 (Fig. 4). The differences between the readings for runs EPA2, EPA3, EPA4 and EPA5 were, 0.5, 0.2, 1.5 and 0.2 ppm, respectively. The difference between the USEPA value measured by the two UKAS accredited labs was 0.9 ppm, *i.e.* the difference in reading between the two accredited labs was more than the average difference between the FTIR and USEPA values. Cl^- (assumed to originate from Cl_2) was found in the NaOH impingers, although this related to an original Cl_2 concentration which did not exceed 0.7 ppm (Table 1).

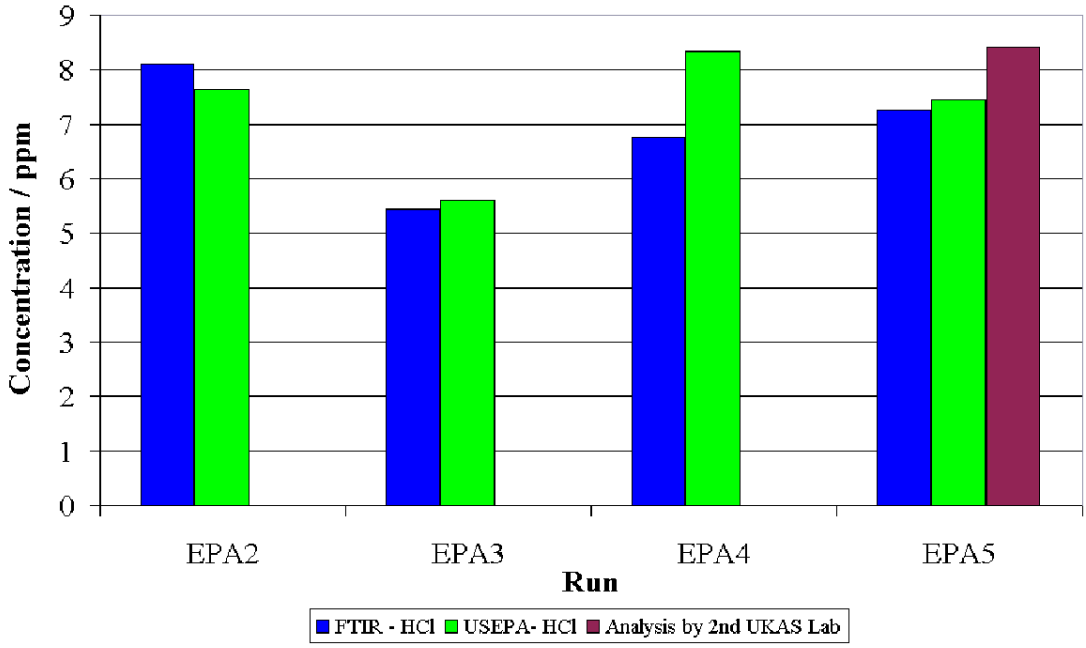

Fig. 4 *Dry HCl measurements performed using both FTIR and USEPA 26 methods. White cell conditions as detailed in Fig. 2.*

Run	Dry Cl_2 concentration / ppm
EPA2	0.5
EPA3	0.7
EPA4	0.7
EPA5	0.6 0.7 (2^{nd} UKAS lab)

Table 1 *Chlorine concentrations.*

The correlation between the contractors' in-house wet chemical technique and the FTIR reading (Fig. 5) was not as close as for the USEPA values. For runs IH1, IH2, IH3 and IH4 the differences were 2.9, 3.2, 1.5 and 2.9 ppm, respectively. [It should be noted that the in-house method simultaneously dissolved HCl and Cl_2 in the H_2O_2 so that differentiation of these species was not possible]. The values reported by the two UKAS labs (9.4 *vs.* 6.9 ppm) again demonstrated that the variability between accredited labs was of the same order, if not greater, than the variability between the FTIR and the wet chemical methods in general.

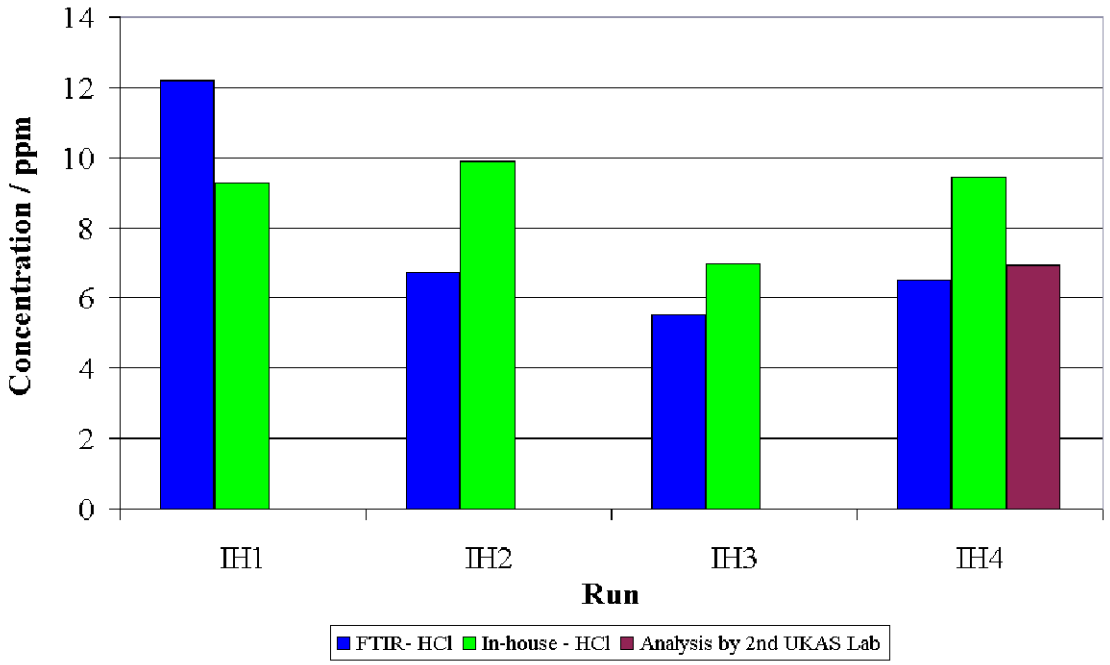

Fig. 5 *Dry HCl measurements performed using both FTIR and the contractors' in-house methods. White cell conditions as detailed in Fig. 2.*

Comparing FTIR and Wet Reference Method Measurements of HF.

Comparing measurements it was found that the difference between the FTIR and USEPA (F^- being assumed to originate from HF) readings were 5.4% and 10.2% for runs EPA2 (1,847 *cf.* 1,946 ppm) and EPA5 (2,146 *cf.* 1,928 ppm), respectively (Fig. 6). In contrast, for runs EPA3 (772 *cf.* 1,736 ppm) and EPA4 (826 *cf.* 2416 ppm) the difference was 124.9% and 192.5%, respectively. The analysis of EPA5 performed by the 2nd UKAS lab gave a value of 2,383 ppm, 11.0% and 23.6% higher than the FTIR and USEPA methods, respectively. Some F^- was found in the NaOH impingers (Table 2), it is possible that due to the high levels present some of the HF may have escaped trapping by the H_2SO_4 pots.

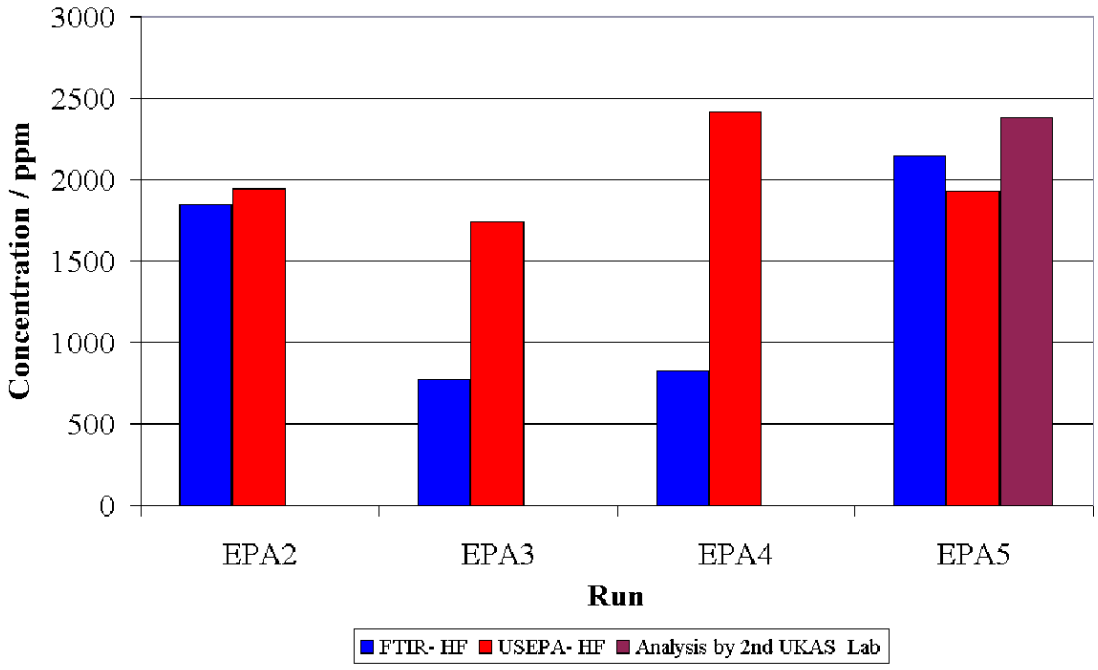

Fig. 6 *Dry HF measurements performed using both FTIR and USEPA 26 methods. White cell conditions as detailed in Fig. 2.*

Run	Dry F^- concentration / ppm
EPA2	1.8
EPA3	2.4
EPA4	4.2
EPA5	2.2

Table 2 *Fluoride concentrations.*

The readings from the contractors' in-house method for HF appear to be spurious (Fig. 7). The contractor has claimed that previously this technique has worked effectively. Clearly, there was some repeated abnormality for each of the four runs, which at present can not be explained.

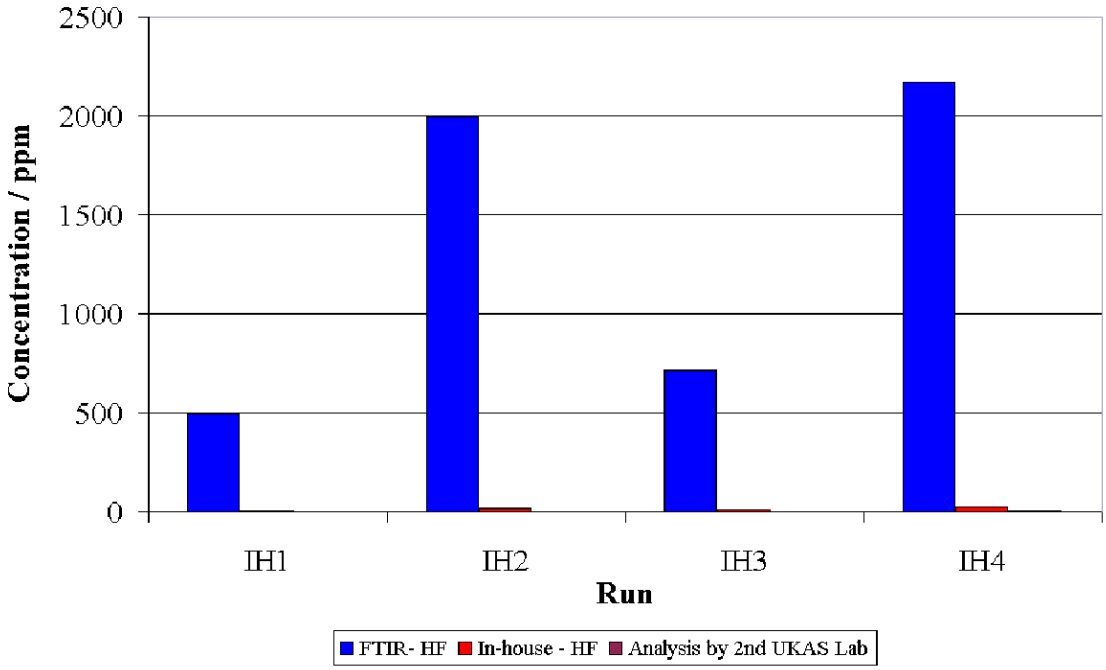

Fig. 7 *Dry HF measurements performed using both FTIR and the contractors' in-house methods. White cell conditions as detailed in Fig. 2.*

Comparing FTIR and The Contractors' In-House SO_2 Measurements.

The FTIR result was higher than the in-house method by 36.3%, 35.4%, 36% and 43.4% for runs IH1, IH2, IH3 and IH4, respectively (Fig. 8). The parallel analysis carried out by a second UKAS lab for IH4 was within 2.4% of the contractors' analysis.

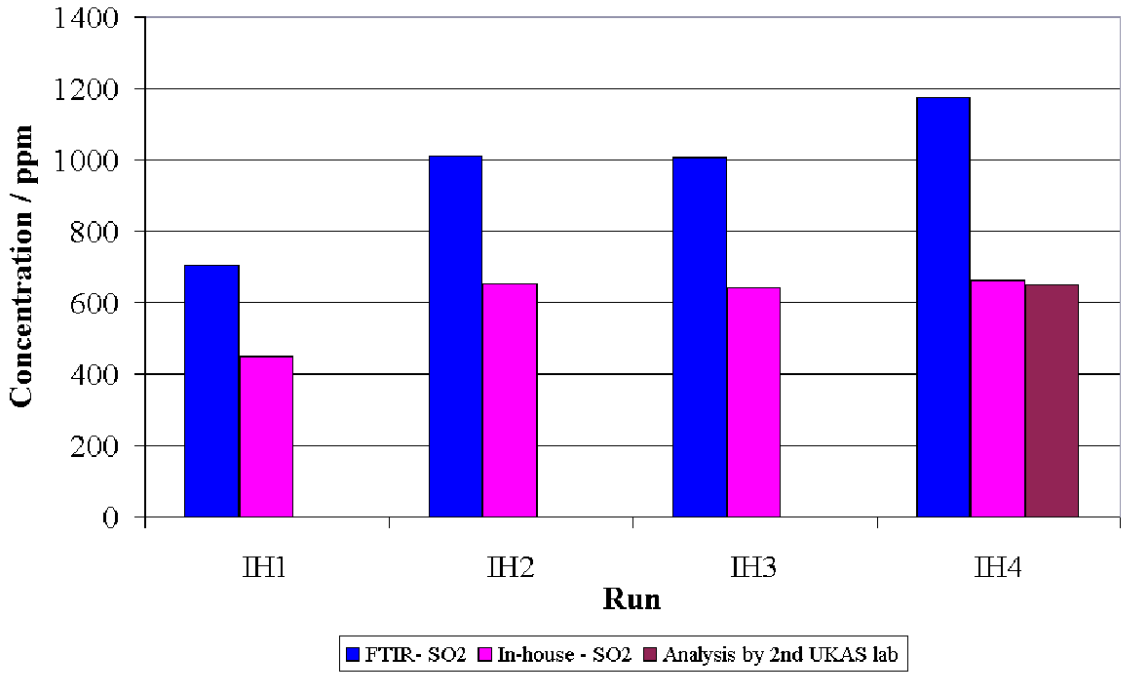

Fig. 8 *Dry SO_2 measurements performed using both FTIR and the contactors' in-house methods. White cell conditions as detailed in Fig. 2.*

Discussion.

By determining the degree of validity of the concentration values of HCl and SO_2 reported by the commercial software, in turn, conclusions can be drawn as to the validity of the wet chemical readings. The various stages of modelling the HCl lines in a measured spectrum recorded on Wednesday 10/07/02 at 16:16 are shown in Figs. 9 – 12. Scaling the HCl model to fit the measured spectrum with water interference removed (Fig. 10) predicts an HCl concentration of 6.4 ppm. This corroborates the value reported by the commercial software which reported 5.8 ppm for the same dataset (Fig. 2). When the combined H_2O and HCl model is compared to the measured spectrum (Fig. 11) the slight baseline drift evident in all the graphs (Figs. 9 – 12) is seen. This is not a consequence of the fitting routines but rather due to the modelled background fit. However, this drift is not sufficient to significantly affect the accuracy of the modelling as evidenced by the residual graph plotted in Fig. 12.

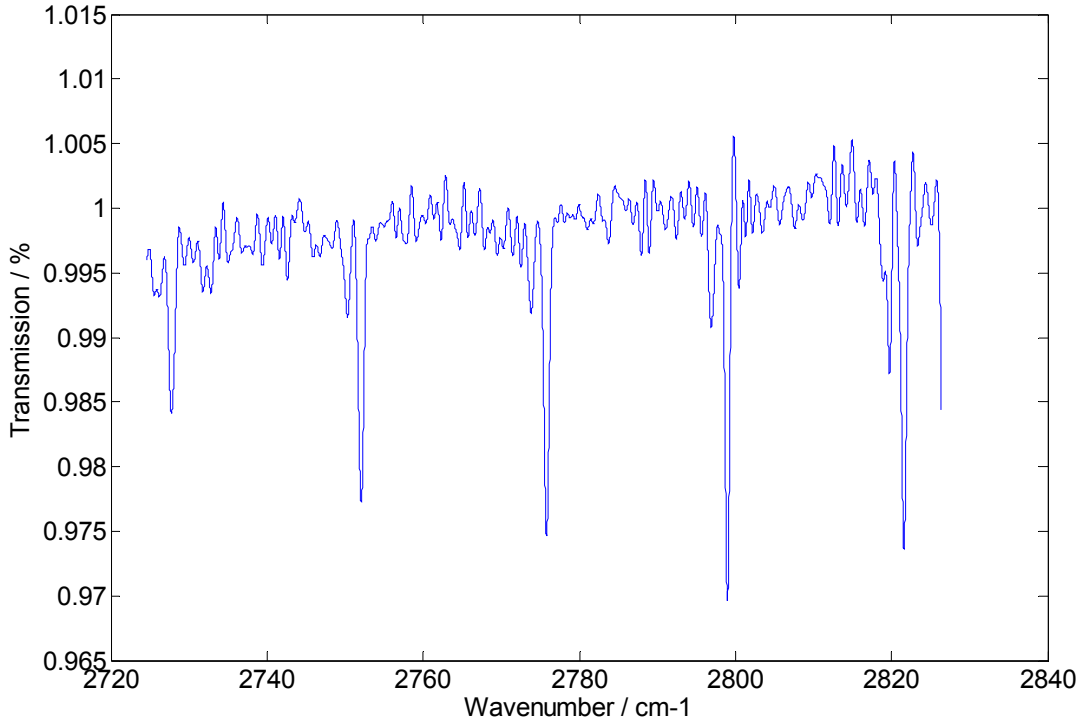

Fig. 9 *HCl absorbencies subsequent to H_2O modelling and removal from a measured spectrum recorded on 10/07/02 at 16:16.*

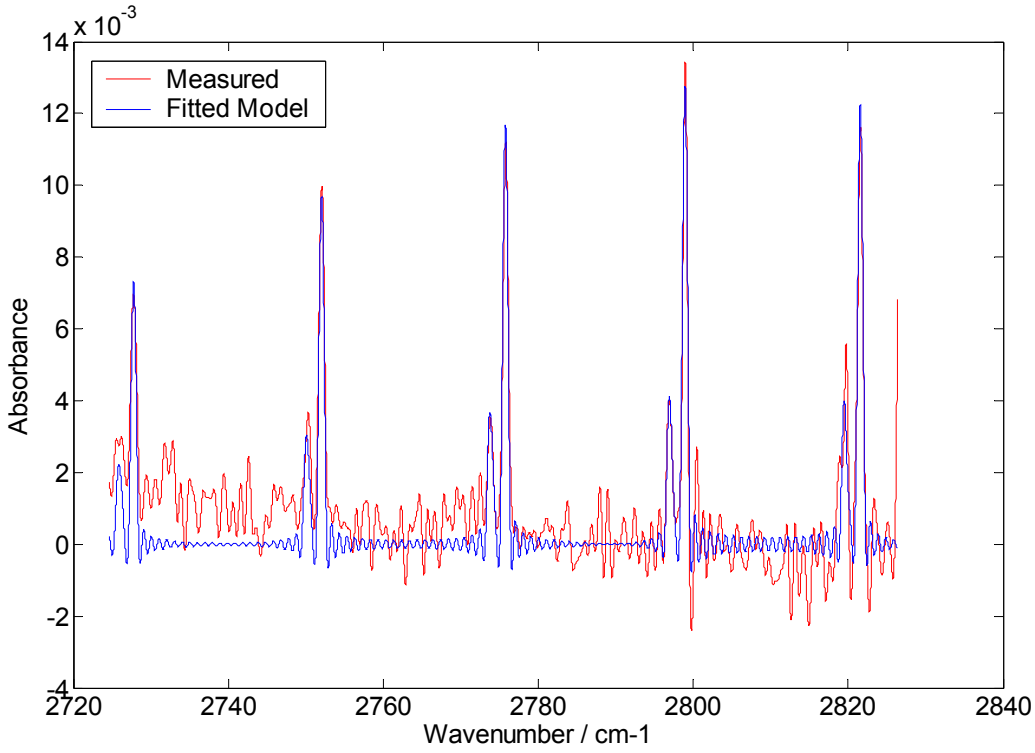

Fig. 10 *Fitting of HCl model to measured HCl absorbencies (from Fig. 9).*

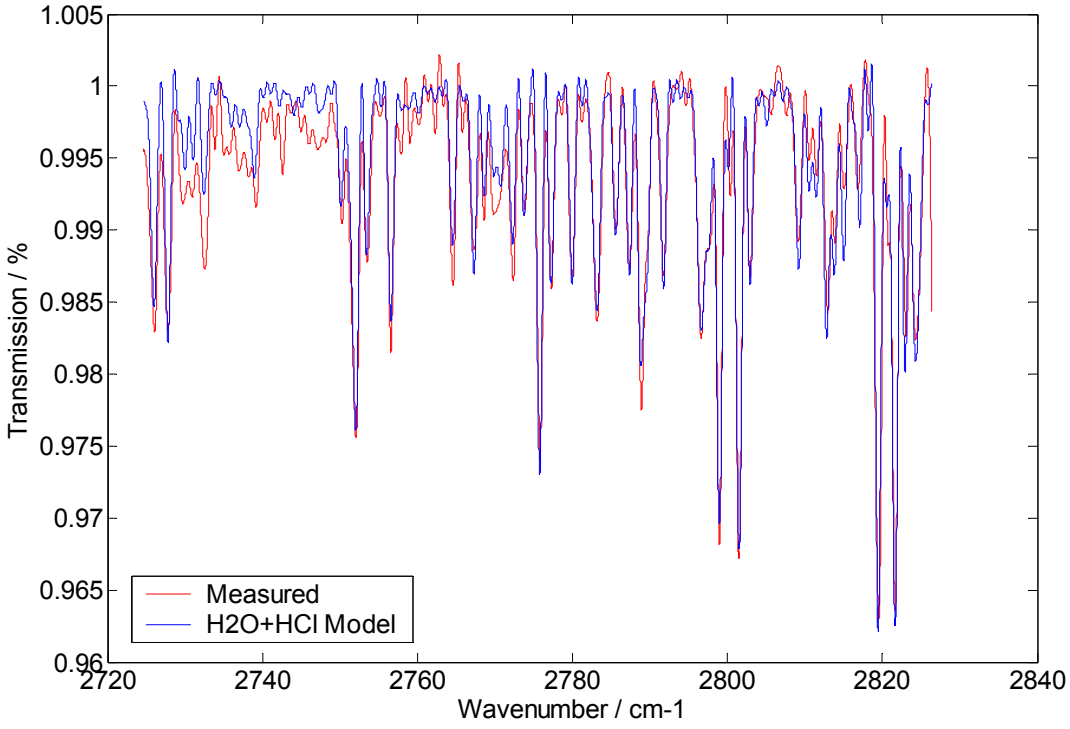

Fig. 11 *Comparison of combined fitted HCl and H_2O models to measured spectrum.*

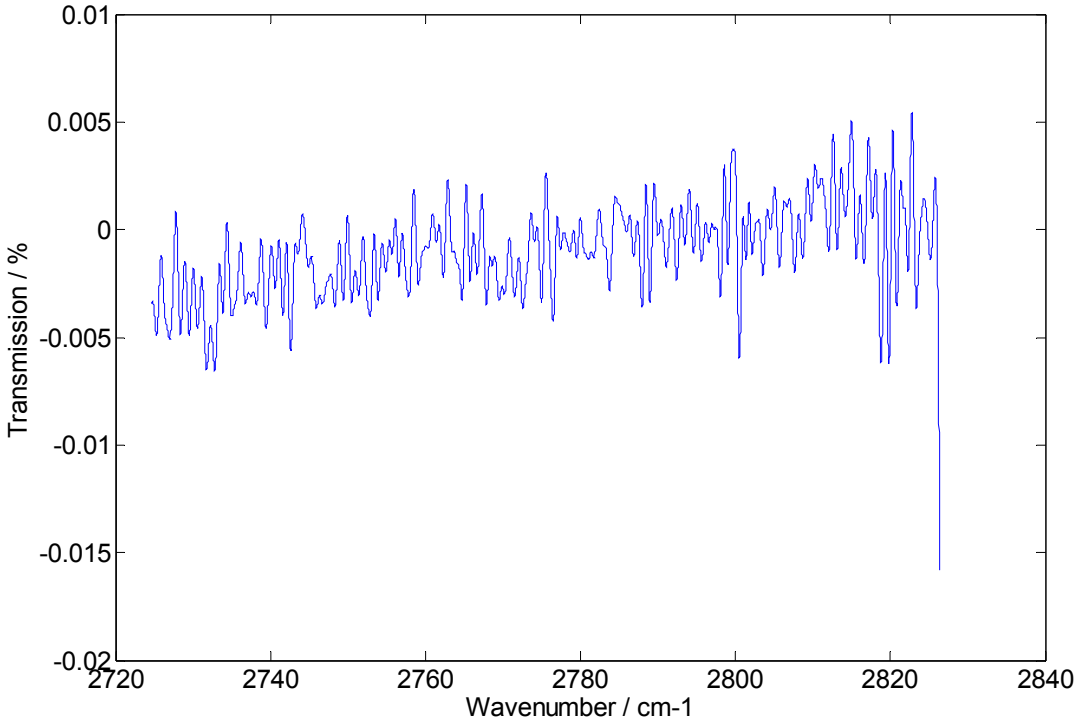

Fig. 12 *Residual of combined HCl and H_2O model subtracted from measured spectrum.*

The correlation between the FTIR and USEPA values for HCl (Fig. 4) is marginally better than for the contractors' in-house method (Fig. 5). In principle this is to be expected as the HCl value for the USEPA method is derived from the total amount of chloride found in the sulphuric acid impingers, which will not dissolve chlorine (the chlorine being dissolved in the subsequent impingers containing sodium hydroxide). In contrast, chlorine is soluble in hydrogen peroxide, which is employed in the in-house method. Hence, the total chloride found in these impingers is derived (at the very least) from both hydrochloric acid and chlorine. Moreover, it is known that small amounts of chlorine are present in the flue gas (Table 1). Hence, the fact that the in-house method reads higher than the FTIR for runs IH2, IH3 and IH4 may be explained in terms of the chlorine contribution to the in-house reading. However, it should be noted that the uncertainties associated with wet chemical methods are in the order of +/- 25%. Hence, with these uncertainties the data cannot be used as evidence for this theory.

It is proposed that the only chlorine based compounds present in the flue are HCl and Cl_2. Since if this was not the case the total chloride measurements from either of the wet chemical methods would be expected to be significantly higher than the FTIR HCl measurement. It is important to note that this conclusion is only true for chlorine-based compounds which are soluble in any of the impinger solutions, which many are.

The above rationale is not mirrored in the data gathered when monitoring HF. Whilst there appeared to be some degree of correlation between the FTIR and USEPA methods for runs EPA2 and EPA5 (Fig. 6), the value reported by the former technique for runs EPA3 and EPA4 is significantly lower. From the latter pair of runs (EPA3 and EPA4) there would appear evidence to suggest that some unknown fluoride is being dissolved in the sulphuric

acid. However, this does not explain why the fluoride readings for the USEPA method on runs EPA2 and EPA5 are also not significantly higher than for the FTIR measurement of HF.

It is not possible to draw any conclusions from the inter-comparison between the FTIR and the in-house method for measuring total fluorides. Clearly, there was some degree of method failure for each of the four runs which at the moment is difficult to explain. The contractor has been unable to explain this since normally HF is detected with this technique. Moreover, they asked the UKAS lab to analyse the samples from each run a second time and the same results were reported again.

Modelling of HF is a complex problem since there are linearity issues with the use of the Beer-Lambert law in the spectral region which would ideally be used for analysis on the low resolution instrument employed. Further development of HF models is an area of continued research at NPL.

By selection of the appropriate wavenumber region water interference with SO_2 can be avoided which allows SO_2 to be modelled. In contrast to HCl, the SO_2 modelling does not support the value reported by the commercial software. The best fit of an SO_2 model to the measured spectrum (Fig. 13) is for a concentration of 462 ppm, *cf.* ~ 650 ppm reported by the commercial software at the coincident time (Fig. 2). Hence, the modelled value was lower than the commercial value by approximately 28.9%.

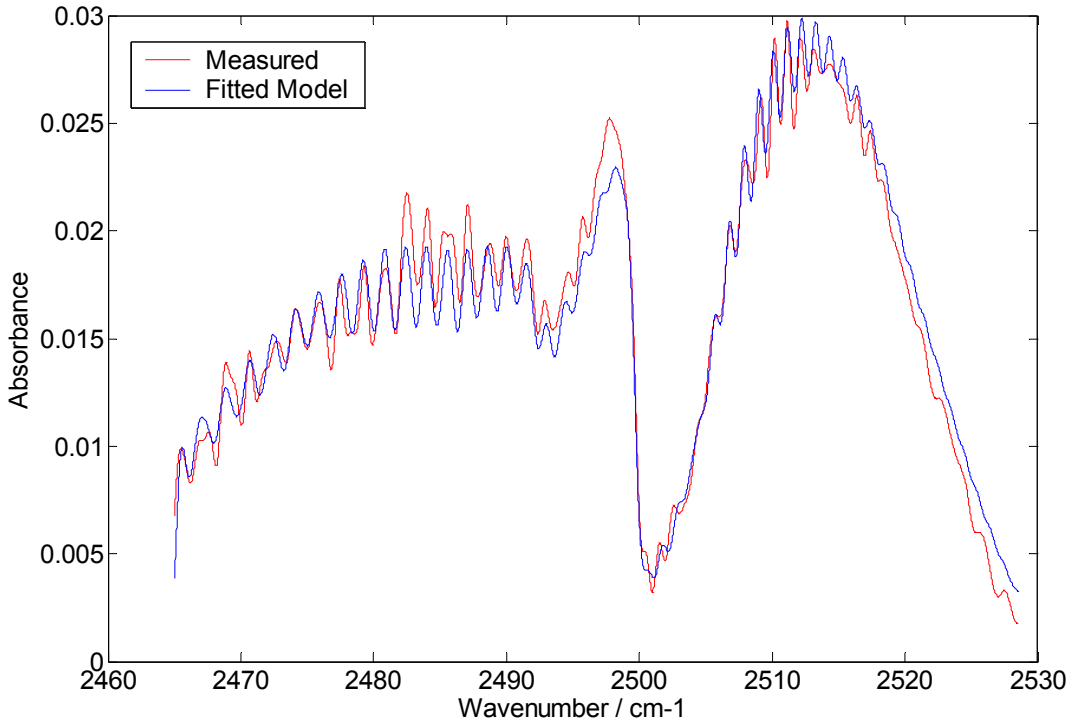

Fig. 13 *Fitting of SO_2 model to measured SO_2 absorbencies.*

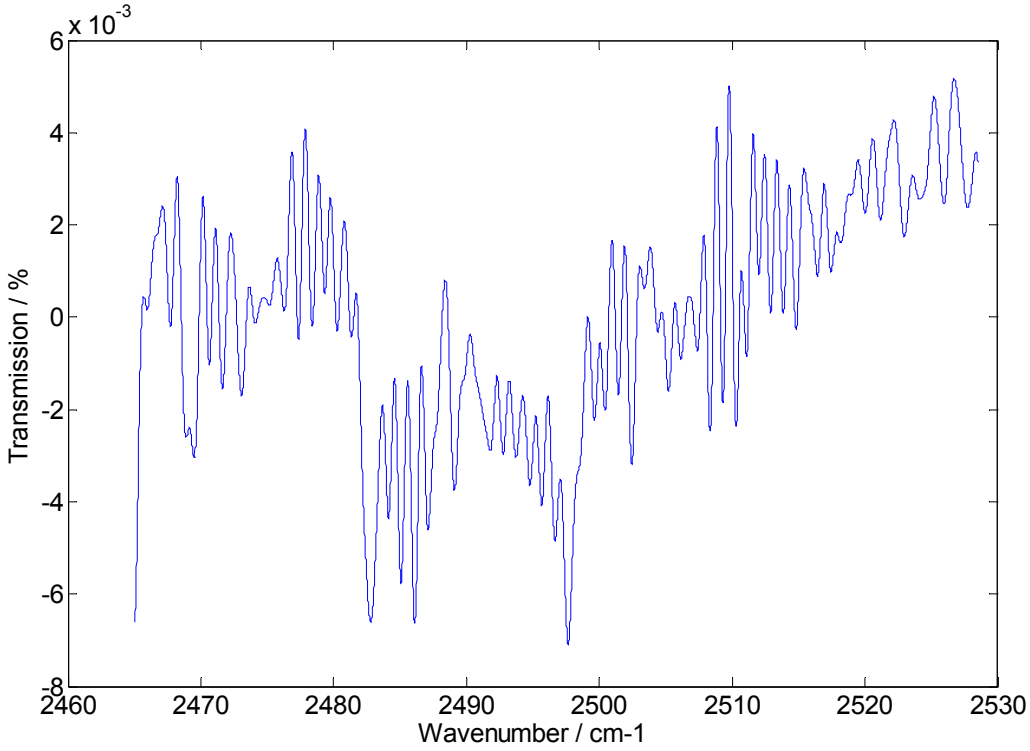

Fig. 14 *Residual of SO_2 model subtracted from measured spectrum.*

In addition, support for this is found when examining SO_2 concentrations reported by the contactor employing their in-house method (Fig. 8). Interestingly, the wet chemical method value was lower than that reported by the FTIR commercial software by 36.3, 35.4, 36.0 and 43.4%. Although these percentages are a little higher than the percentage difference between the model and the commercial software value, there is none the less clearly a consistent trend.

Conclusions.

It has been shown that FTIR spectroscopy can be employed for multi-species analysis, on-line in real-time. Both USEPA 26 and contractors' in-house methods have been shown to produce corroborating results to FTIR for HCl quantification. In contrast, a close correlation between FTIR and USEPA 26 measurements was not found for the determination of HF concentrations. This disagreement may have been due to the presence of an unknown fluoride based species soluble in aqueous sulfuric acid.

The modelling of the recorded FTIR spectra has validated the measurements reported on plant. Furthermore, given that steam is a well known interferent in FTIR spectra an important part of the validation was the demonstration that even in the presence of a relatively large amount of steam the correct concentrations were reported by the instrumentation.

Economic and Operational Benefits to the Plant.

It costs the plant ~ £35k p.a. for external contractors to monitor all the species mentioned in this report across two stacks. The plant also has to pay the Environment Agency to send their contractors in to perform measurements at a cost of ~ £3.5k p.a. Their own in-house monitoring costs a further £6.5k, plus some additional maintenance costs. For an initial outlay of ~ £50k an FTIR could be purchased and run in-house, saving an estimated £27k per annum, representing a 2 year payback on the initial investment. In addition to this economic benefit there are also operational advantages. For example, since there is a relationship between the furnace temperature and NO_x emissions a real-time instrument like FTIR could be used optimise the furnace flame temperature through profiling the NO_x release.