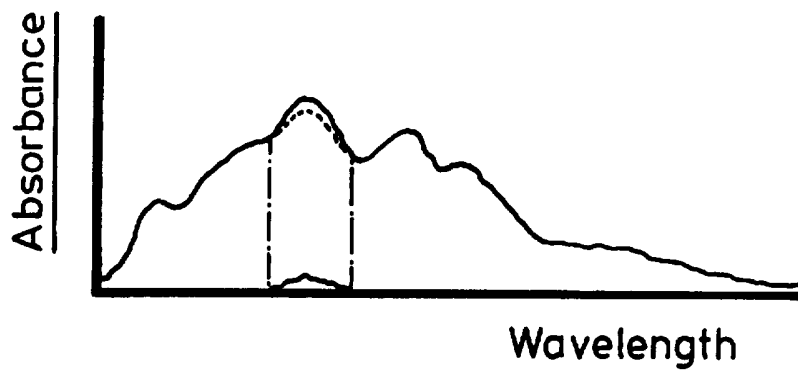




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(54) Title: QUANTITATIVE DETECTION OF CHEMICAL SPECIES**(57) Abstract**

A method and apparatus for determining the concentration of a target chemical species in a sample. A first spectrum is generated representing the absorbance of the sample across a range of wavelengths. The sample is then exposed to conditions which modify the concentration of the target chemical species in the sample, for example by irradiating the sample with UV or visible light which degrades the target chemical species, or generating an active species flux through the sample by exposing the sample to a corona discharge. The absorbance of the sample is then remeasured across the same range of wavelengths and differences between the two spectra are analysed to quantify the concentration of the target chemical species in the unmodified sample.

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QUANTITATIVE DETECTION OF CHEMICAL SPECIES

This invention relates to a method and apparatus for the quantitative detection of chemical species.

It is desirable to be able to determine the quantities of chemical species present in a sample, for example, to measure the amount of chlorine disinfectant present in water. Chlorine disinfection is most commonly effected using gaseous chlorine or sodium hypochlorite. Both methods of disinfection initially produce hypochlorous acid (HOCl) which then dissociates to OCl^- and H^+ ions. The concentration of each ion is a function of the pH and temperature of the solution, and probably also of the water's background history and other chemical constituents. The presence of two species of disinfectants of different strengths is the main difficulty in chlorine disinfectant measurement, and ideally each species should be measured independently.

One method of measuring the quantity of different species in a water sample is ultraviolet (UV) spectroscopy, which measures the transmission of a beam of light through a parallel-sided cell containing the sample. A fraction of the light is absorbed by the sample, with each species in the sample absorbing light at a characteristic wavelength. The absorption curves of HOCl and OCl^- show strong absorption features at about 235nm and 292nm. However, in addition to the peaks of interest, the sample may contain other species with characteristic absorption peaks, for example, chloramines (added deliberately to the water in some circumstances to provide a long-lasting disinfectant residual) at 254nm, SO_2 , O_3 , and aluminium- and ferric-based coagulants. Further, particles present in the water such as colloids and bubbles, etc, give rise to a featureless apparent-absorption spectrum which causes severe baseline shifts in all spectra, making true absorption measurements more difficult.

It is thus very difficult to determine the concentration of the HOCl species (and to a lesser extent the OCl^- species) in the presence of high concentrations of nitrate, monochloramines and other contaminants in tap water.

It has been proposed to use the technique of difference spectroscopy to reduce the effects of background interference. One proposal (R. Briggs et al, "On-line monitoring of residual chlorine" Journal of Water Science and Technology 10, 39-49 (1990)) uses chemical addition to adjust the sample pH and hence change the relative concentrations of HOCl and OCl⁻ between single-wavelength absorption measurements. However, this technique is inconvenient to apply and removes the primary advantage of spectroscopic techniques, namely reagentless operation.

British Patent No. 1570236 describes a method for detecting the presence in a sample of photochemically modifiable constituents such as cannabinoids, the method relying upon high pressure liquid chromatography. HPLC is capable of very effectively separating a target constituent such as cannabinoid from the other constituents of a complex mixture. This is the source of the technique's high selectivity. However, the separated constituent may be difficult to detect. For example, cannabinoid is invisible (because of inconveniently low optical absorption) to a single-wavelength photometric detector. In order to improve the sensitivity with which the appearance in the chromatograph eluent of a target constituent can be detected, the target constituent is modified photochemically by irradiation with light. Depending upon the nature of the target species, the photochemical modification may convert the target constituent to a species having different fluorescent characteristics, or different light absorbance at a particular wavelength. Selectivity may be increased by comparing measurements of fluorescence, intensity or absorbance strength taken from modified and unmodified samples. Data to be compared can be generated either by temporarily discontinuing the photochemical modification of the eluent stream passing through a single detector, or by passing a stream through two detectors arranged in series and photochemically modifying the stream at a point between the two detectors.

The method of British Patent No. 1570236 is useful in circumstances where HPLC effects good separation of a target species from a mixture, but the separated eluent is difficult to detect in the output stream detector, or further improvement of selectivity is needed. Where the mixture cannot easily be

separated chromatographically (as in water monitoring) the optical measurements themselves must provide the selectivity. For the reasons outlined above such optical measurement selectivity is very difficult to achieve.

It is an object of the present invention to obviate or mitigate the abovementioned problems.

According to the present invention, there is provided a method for determining the concentration of a target chemical species in a sample, wherein the absorbance of the sample is measured across a range of wavelengths to produce a first absorbance spectrum, the sample is exposed to conditions which modify the concentration of the target chemical species in the sample, the absorbance of the sample is re-measured across the said range of wavelengths to produce a second absorbance spectrum, and differences between the two spectra are analysed to quantify the concentration of the target chemical species in the unmodified sample.

The concentration of the target chemical species, and hence the optical spectrum, may be modified by photolysis, by photolysis in combination with a photoconductor (e.g. TiO_2) capable of generating highly reactive species such as OH radicals, or by injecting similar reactive species into the sample from a high voltage corona. Where further selectivity of target quantification is desired, these techniques may be combined to produce a set of modified spectra which together unambiguously characterise the target species.

The present invention is based on the realisation that it is possible to highly selectively quantify the concentration of target chemical species through analysis of small absorbance changes effected by modification of the target's absorbance spectrum. The use of full spectral information, combined with chemical modification of the target, provides a double "signature" characteristic of the target species. Under ideal circumstances, which are approached in many useful situations, the target species is modified without any other constituent of the sample being modified. However, even if a constituent other than the target is also modified, it is highly unlikely that this will generate a similar "signature" and therefore appropriate spectral analysis will in most circumstances be capable of accurately quantifying the target.

The sample may be photolytically modified by exposing it to UV or visible light generated by a continuously or intermittently operating light source. Alternatively, a corona discharge may be generated by applying a voltage between a first electrode spaced from the sample and a second electrode immersed in the sample. A grounded electrode may be positioned between the first electrode and the sample to remove charged species.

The invention also provides an apparatus for determining the concentration of a target chemical species in a sample, comprising a spectrometer for making successive measurements of the absorbance of the sample across a range of wavelengths to produce at least two absorbance spectra, means for exposing the sample to conditions which modify the concentration of the target species in the sample, and means for comparing spectra generated before and after exposure of the sample to quantify the concentration of the target species.

Specific embodiments of the present invention will now be described, by way of example only, with reference to the accompanying drawings, in which:

Figs. 1 and 2 show absorbance spectra for two samples, modifications to the spectra resulting from photolysis, and the difference between the modified and unmodified spectra;

Fig. 3 shows conventional spectra of some common disinfectant species and tap water;

Fig. 4 shows reduction of the OCl^- absorption peak following irradiation with a low-pressure mercury lamp;

Fig. 5 shows the spectral modulation due to a series of flashes from a xenon flash lamp for an acidic solution of chlorine (mostly HOCl species present);

Fig. 6 shows the difference spectra according to the present invention for a single concentration of chlorine at different pH values and for a tap water sample;

Fig. 7 shows the difference spectra in alkaline conditions for a series of chlorine concentrations from 0.75 ppm to 16 ppm.

Fig. 8 is a sectional side view of a corona discharge cell used in accordance with an embodiment of the present invention;

Fig. 9 is a section through Fig. 8 on line 9-9;

Fig. 10 illustrates the change in absorbance at various wavelengths with a hypochlorite-containing water sample with successive corona irradiations;

Fig. 11 illustrates absorbance versus wavelength for a sample containing methylene blue with successive corona irradiations;

Figs. 12 and 13 illustrate absorbance difference versus wavelength resulting from photolytic degradation for nine calibration samples; and

Figs. 14 and 15 illustrate calibration data derived from the absorbance differences represented in Figures 10 and 11.

Fig. 1 shows in full line an absorbance spectrum including background effects generated from a water sample. The broken line represents a spectrum taken from the same sample after a target species has been subjected to photolytic degradation. A further full line represents the difference between the two spectra. Fig. 2 shows equivalent curves for a water sample in which photolysis results in a more complex modification of the spectrum. The present invention is based on the realisation that analysis of the "difference" spectrum makes it possible to quantify the concentration in the sample of the species which is affected by photolysis.

Figs. 3 to 7 show the results of experiments to determine the feasibility of the method of determining the concentrations of chlorine disinfectant present in a sample of water according to the present invention.

The experiments were conducted using conventional UV spectroscopy equipment. Light from a deuterium lamp was shone through the sample, which was placed in a 10mm path length UV-silica cuvette. The deuterium lamp typically produces a continuous, line-free spectrum in the range 160-360nm. The emitted radiation density varies from a few $\text{mWcm}^{-2}\text{nm}^{-1}\text{sr}^{-1}$ to a tenth of this over this range. Typical lamps are operated at 80-100V at a current of 300mA after a heating and ignition phase.

After the light has passed through the sample, it is detected across the range of wavelengths of light emitted by the lamp to obtain absorption spectra using a wavelength dispersing grating and a detector array.

Figure 3 shows conventional spectra of some common disinfectant species. The peaks of HOCl and OCl⁻ are easily identified in the spectra, showing strong absorption features at about 235nm and 292nm. A monochloramine absorption is also visible in the curves, overlapping the HOCl absorption, but slightly displaced at 254nm. A tap water spectrum is also shown in Fig. 3.

Because of the wide variation of species present in tap water, it is very difficult to produce spectra which have easily identifiable peaks. It is also difficult to determine the concentration of the HOCl species (and to a lesser extent the OCl⁻ species) in the presence of high concentrations of nitrate in the water (the nitrate having an absorption edge below about 240nm), or high concentrations of monochloramine and other interferents.

The present invention is based on the realisation that what is needed is to determine small changes in spectral shape which are superimposed on large interfering absorption features. Thus, in order to highlight these spectral changes two spectra are measured, one for the sample as first obtained and one with the species of interest modified by for example being at least partially removed. One method of removing the chlorine species could be adsorption onto activated carbon but this would not be convenient at low sample flow rates because of the large volume of carbon required and the detrimental affect this has on sampling times.

A more effective method is to expose the sample to conditions in which the chlorine species are at least partially removed. This may be achieved by irradiating the sample with light. Initial experiments with a low-pressure mercury lamp (wavelength = 254nm) showed (Fig. 4) that irradiation for long periods of time can be used to reduce the absorption of the 292nm absorption feature progressively (71% reduction in 35 minutes). Fig. 4 shows eight curves representing the spectrum after successive intervals of 5 minutes. However, a very rapid before and after irradiation measurement cycle is desired to reduce

drifts in background spectra due to other causes, so a xenon flash-lamp system was investigated.

The sample was irradiated in a 10mm path length UV-silica cuvette placed within the reflector of a commercial photographic flash unit. Using a charger, the energy per flash was set at 45J. The cycle-time was 10 seconds, and five flashes reduced the OCI^- concentration measured by its 292nm absorption peak by 65%. Similar but slightly smaller reductions in the HOCl absorption feature were also measured. Whilst this percentage reduction is not as large as desired, it is adequate for many measurements.

In the procedure, a first spectrum was measured and the cuvette was removed to a separate irradiation apparatus before being returned to the spectroscopy equipment for remeasurement. Using this procedure can introduce errors into the measurements, as even small changes in the orientation of the cuvette in the spectrometer can cause apparent absorption changes. A fixed procedure with irradiation in situ is thus preferable.

Fig. 5 shows the spectral modulation due to a series of xenon flash-lamp flashes for an acidic solution of chlorine (mostly HOCl species present). Alkaline spectra were similar to those of Fig. 4 and are not illustrated. Fig. 6 shows the difference spectra (i.e. differences between subsequent spectra and the original spectrum) for a single concentration at different pH values. The two spectral features at 235nm and 292nm are clearly visible. Fig. 7 also shows the difference spectrum for a tap water sample, showing very little change with irradiation, except below 205nm. Some of the remanent modulation, especially visible as a shift at long wavelengths, is due to a temperature increase after flashing. This was measured to be 4.2°C using a small thermistor as a probe, immersed in the sample. It is possible that sample heating could be reduced by isolating the cuvette from the heat of the flash-tube and by using a cold-mirror or filter arrangement, reducing the irradiance at wavelengths above 400nm. Software correction using a direct temperature measurement may also be an option for improvement.

Fig. 7 shows the differential response in alkaline (predominantly OCl^- present) conditions for a series of concentrations from 0.75 ppm to 16 ppm. Real spectral modulation, even in tap and de-ionised water samples, does occur at wavelengths less than 205nm under irradiation. It is not known what chemical reactions are taking place, but this suggests that the short wavelength region should be excluded from any analysis. The photolytic reactions are presumed to convert HOCl and OCl^- to chloride ions. This may significantly change the pH, complicating interpretation of the two spectral features.

The deuterium lamp used for the UV spectroscopy could also be used for the dechlorination as well as for spectroscopy, particularly using a fixed system with irradiation in situ.

The primary limitation of the deuterium lamp is its operating life. Typically, an operating life of 2000 hours at rated drive before a gradual reduction in output to 50% of its initial value is claimed by the manufacturers. Such a short lifetime before replacement of the lamps becomes necessary would represent a disadvantage similar to that of reagent replacement in the prior art. However, lifetime of the lamps appears to be a rapid function of operating current, so it is possible that power management with a low operating power state between measurement phases would extend the life beyond 5000 hours.

Medium and high pressure mercury lamps provide a line spectrum of high intensity and could be useful if a suitable wavelength was located. Xenon arc lamps have lower efficiencies but exhibit reduced line structures. Time resolved spectral measurement and simultaneous dechlorination are possible with a xenon flash lamp. Metal halides lamps may also be used but are only available in very high power types. Higher efficiencies could be expected from excimer sources, either as lasers or as incoherent discharge lamps. Many line spectra are available from excimer sources, such as ArF (193nm), KrCl (222nm), KrF (248nm), XeCl (308nm) and XeF (351nm) amongst others. A series of such excimer sources in the form of small-sized lamps may be very useful in performing the method according to the present invention.

The investigations described above suggest that rapid dechlorination (and removal of certain other species) using a very intense but short photolytic irradiation from a flash lamp may be the best method of carrying out the invention. However, the chlorine species could alternatively be removed by continuous irradiation by, e.g. a mercury arc lamp, deuterium lamp or an excimer lamp.

The target chemical species may be modified by exposing the sample to conditions other than photolytic degradation. For example, the characteristics of the sample may be modified by passing through it an active species flux generated by a corona discharge. Figs. 8 to 11 illustrate embodiments of the invention which rely upon corona discharge.

Referring to Figs. 8 and 9, the illustrated spectroscopic cell is formed from fused quartz and has four planar side walls 1 of equal length and width and a base 2. Three loops 3 of 100 micrometer diameter platinum wire are glued onto the base, the wire being passed out of the cell between the base and one of the side walls. The cell defines an internal space 40mm deep and 10mm wide. The cell was mounted in the optical path of a spectrometer (not shown), the spectrometer used in experiments being a Hewlett-Packard 8452A diode array spectrometer. The optical path of the spectrometer is indicated in Fig. 8 by the arrow 4.

The wires 3 are connected to earth through a microammeter 5 as shown in Fig. 8. Samples were introduced to the cell to a depth of 30mm, giving a sample volume of approximately 3ml. A size 5/10 sewing needle 6 was inserted into the open end of the cell and supported such that the vertical position of its point could be adjusted. During experiments the needle position was adjusted such that its point was spaced from the sample meniscus by a fixed amount. The needle was connected by a high voltage cable to the negative terminal of a DC generator (not shown). The generator comprised a 30 kHz transistor and ferrite transformer oscillator generating approximately 1200 volts peak to peak and supplying a multi-stage Cockroft-Walton type voltage multiplier capable of delivering a variable voltage of up to 8 kV.

Samples of aqueous chlorine were made up from stock 14% sodium hypochlorite solution, diluted to the ppm concentration level, and adjusted in pH using sodium hydroxide and hydrochloric acid. These were pipetted into the spectrometer cell and the corona electrode was adjusted in height to give a 4mm gap between the needle point and the meniscus.

An initial spectrum was measured for each sample before a voltage was applied to the needle. This measurement was used to establish the absolute sample absorption, but primarily to establish a reference for subsequent measurements. For each subsequent measurement of the same sample, the absorption at each wavelength was compared with the reference absorption and the difference was recorded. Thus attention was focused on changes in absorption rather than absolute values of absorption.

Fig. 10 shows results obtained with a chlorinated water sample repeatedly exposed to a corona wind. Zero absorbance difference corresponds to the reference spectrum taken before initiation of a first corona discharge. The spectrum for each of the 13 subsequent measurements is shown in Fig. 10, the first subsequent measurement being taken 30 seconds after initiation of the first corona discharge but before initiation of the second corona discharge, and the other measurements being taken at 15 second intervals thereafter during intervals between successive discharges. When the corona current was flowing, the surface of the meniscus was visibly dented by the corona wind, and caused to move around actively. It is believed that this aids mixing in the confined spectrometer cell. Fig. 10 shows a steady decrease in the absorption strength of the main 292nm absorption feature of the hypochlorite ion (alkaline pH) and an increase of a strong feature at 220nm. This is represented by the arrows 7 and 8 respectively. This short wavelength feature appears during corona discharge in all samples measured to date, both tap water and distilled water. Its constitution has not yet been determined, but is likely to be a mixture of nitrate ion and nitric acid from oxides of nitrogen.

Determination of the hypochlorite concentration from the results shown in Fig. 10 requires a calibration curve. To obtain this, many samples were prepared and measured using another (reference) analytic technique, that is by

using the indicator DPD. It would have been possible to use alternative techniques, for example titration. Each sample was then exposed to the corona wind for a fixed time and at a controlled current level. The current was regulated by directly measuring it as shown in Fig. 8 and by adjusting the voltage to maintain a constant current. Alternatively, the total charge delivered could have been measured by integrating the current over time, and stopping the current when a predetermined total charge was reached.

After exposure to the corona wind, the absorption spectrum was measured again, and the difference formed. For each sample concentration the spectrum looked like one of the curves of Fig. 10, with high concentrations giving a large value of absorbance difference, and low concentrations small absorbance differences.

With very clean curves such as those shown in Fig. 10, data analysis was very simple. Plotting the peak absorbance difference at 292nm wavelength against the known original concentration gave points distributed closely about a straight line. Hence the absorbance difference was deemed linearly related to the original concentration of the hypochlorite ion. A straight line was fitted to the points by linear regression, and this became the calibration curve.

Once the calibration curve has been determined, two spectral measurements with an intervening exposure to the corona wind allows for estimation of the concentration. Simply reading off the calibration curve from the measured value of absorbance difference at 292nm gives the estimated concentration.

At lower concentrations where the spectra are much "noisier", it is necessary to use more of the spectral information available. This may be achieved using the chemometric technique Partial Least Squares regression (PLS). In PLS the full spectra are analysed together with concentration values obtained by the reference technique. This is termed multivariate regression. In effect each unknown spectrum is filtered using the known form of the absorption spectrum of the hypochlorite ion. Using more spectral information improves the signal to noise ratio of the measurement. This technique is standard practice in spectroscopic instruments.

Fig. 11 shows results obtained for a second sample of water which had been contaminated with the dyestuff methylene blue. As in the case of Fig. 10, the sample is repeatedly exposed to a corona wind and the absorbance is measured between successive exposures. Whereas in Fig. 10 the change in absorbance is plotted for each wavelength, in Fig. 11 the absolute absorbance is plotted against wavelength. The uppermost curve in Fig. 11 (in the range 600-700 nm) corresponds to a measurement made before initiation of the corona discharge. The other curves correspond to measurements made after 30 seconds and at 15 second intervals thereafter. These spectra are more complex than those in the example of Fig. 10, showing a decrease or bleaching of features at 600-700 nm and at 245-290 nm as represented by arrows 9, but a broad increased absorption at 330-480 nm as represented by arrow 10. The large edge below 230 nm is the unknown generated species mentioned above with reference to Fig. 10. Thus in the curves of Fig. 11 we see not only a destruction of a chemical species, but also active chemistry with formation of other, spectrally-differentiated species.

Only one configuration of corona discharge is described above. This used a negative electrode polarity in an air atmosphere. There may be additional advantages in using a positive electrode polarity, in removing the charged species of the corona wind with a grounded grid electrode, and in operating in atmospheres other than air. The technique is also of interest for non-aqueous samples, for gas samples which have UV absorbing features, and with other forms of detection such as infrared spectroscopy.

The method of the invention relies upon the comparison of spectra generated before and after modification of the characteristics of a sample. That comparison may be made using for example the technique of principal component analysis. The application of this technique in the context of the present invention is described below by reference to a worked example.

Raw calibration data were generated from nine samples of water, the samples having the following pH values and concentrations of HOCl and OCl⁻:

Sample	pH	HOCl Concentration	OCl ⁻ Concentration
0	9.0	0	0.01
1	9.0	0	0.25
2	9.0	0	0.51
3	9.0	0	0.71
4	9.0	0	1.15
5	6.0	0	0
6	6.0	0.42	0
7	6.0	0.80	0
8	6.0	1.26	0

For each sample, an absorbance value was measured at each of 200 wavelengths, the n th value being measured at a wavelength of $200 + 2n$ nm. Each sample was then irradiated with light from a low pressure mercury lamp for a continuous period of one minute, and the absorbance at each of the 200 wavelengths was then remeasured. The absorbance spectrum difference was then calculated. The first ten and last fifty measurements contained little information and were therefore discarded. The remaining results for $n=10$ to $n=150$ were then plotted as shown in Figs. 12 and 13.

The data were then offset to one wavelength pivot ($n=120$) for background drift compensation, the data were mean-centred, and the mean-centred data were plotted as shown in Figs. 14 and 15. All the spectral data were then concatenated into a large data-matrix X with 9 rows and 141 columns, each row representing one sample difference spectrum.

Following well known procedures such as are described in Harald Martens and Tormod Naes "Multivariate Calibration", John Wiley, 1993, ISBN 0 471 93047 component analysis was then performed by forming M , the covariance matrix:

$$M := X^T \cdot X$$

where superscript T denotes the matrix transpose. Eigenvectors were then calculated for M, and the largest significant eigenvalue chosen by observation. In this example, the maximum eigenvalue (mx) to use (counting from zero) was selected as:

$$mx:=1$$

“loadings” (P) were then calculated from the eigenvectors of M.

and the “scores” T were calculated:

$$T:=X.P.(P^T.P)^{-1}$$

It was assumed that the expected maximum number of principal components would be 5.

Using the data plotted in Figs. 14 and 15:

$$T = \begin{bmatrix} -0.097 & -0.021 \\ -0.065 & -0.004 \\ -0.03 & 0.022 \\ 0.017 & 0.034 \\ 0.029 & 0.061 \\ 0.058 & -0.02 \\ 0.014 & -0.021 \\ 0.07 & -0.026 \\ 0.121 & -0.025 \end{bmatrix}$$

$$U:=X.P$$

$$S:=(U^T.U)^{-1}.U^T.Y$$

where each row again comes from one calibration sample. The calculations up to now constitute calibration of the measurement system.

An unknown spectrum can then be taken to calculate an estimate of the concentration of HOCl or OCl⁻ (Ypred) in a sample from which the unknown spectrum resulted. First the unknown sample spectra are formed as rows of Runk. The data is centred as before:

$$X_{unk} = (R_{unk}^T - x_m)^T$$

$$U_{unk} = X_{unk}.P \quad Y_{pred} = U_{unk}.S$$

Ypred was calculated on the basis of the nine spectra initially used for calibration purposes to produce the following:

$$Y_{pred} = \begin{bmatrix} -0.38 & -0.3 \\ -0.325 & -0.079 \\ -0.334 & 0.275 \\ -0.168 & 0.454 \\ -0.311 & 0.81 \\ -0.164 & -0.282 \\ 0.24 & -0.273 \\ 0.582 & -0.312 \\ 0.86 & -0.292 \end{bmatrix}$$

This data was then used to estimate the HOCl and OCl⁻ concentrations in the nine samples as follows by reshifting and decentering the data:

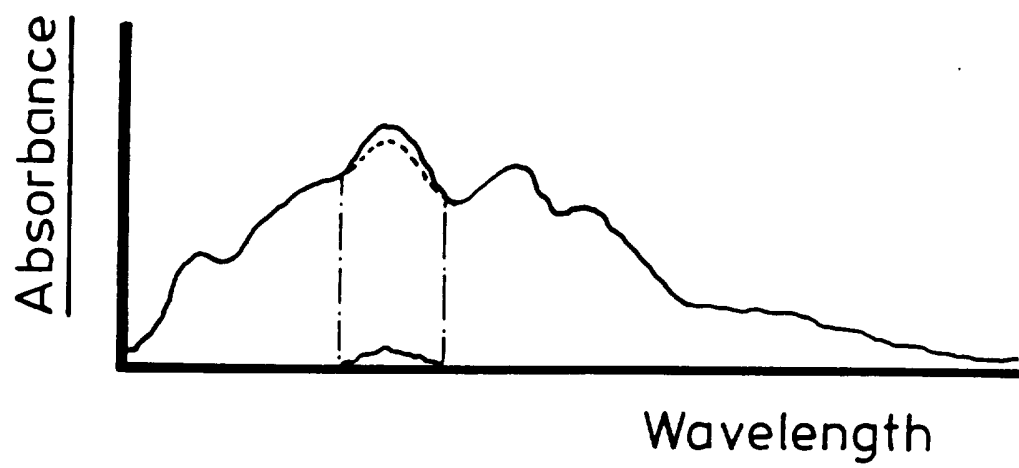
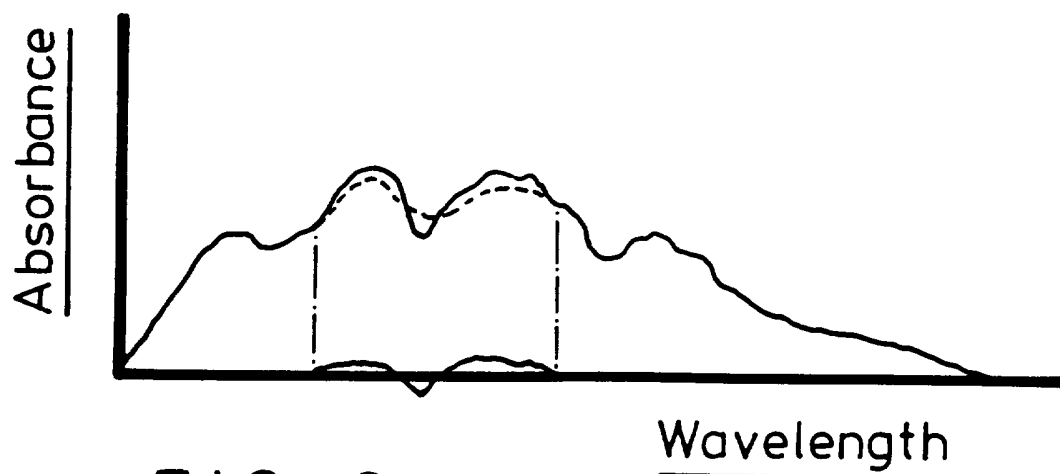
Sample	HOCl Concentration		OCl ⁻ Concentration	
	Estimated	Actual	Estimated	Actual
0	-0.105	0	-0.008	0.01
1	-0.05	0	0.213	0.25
2	-0.059	0	0.567	0.51
3	0.107	0	0.747	0.71
4	-0.035	0	1.102	1.15
5	0.112	0	0.01	0
6	0.515	0.42	0.019	0
7	0.858	0.8	-0.02	0
8	1.136	1.26	-0.00014	0

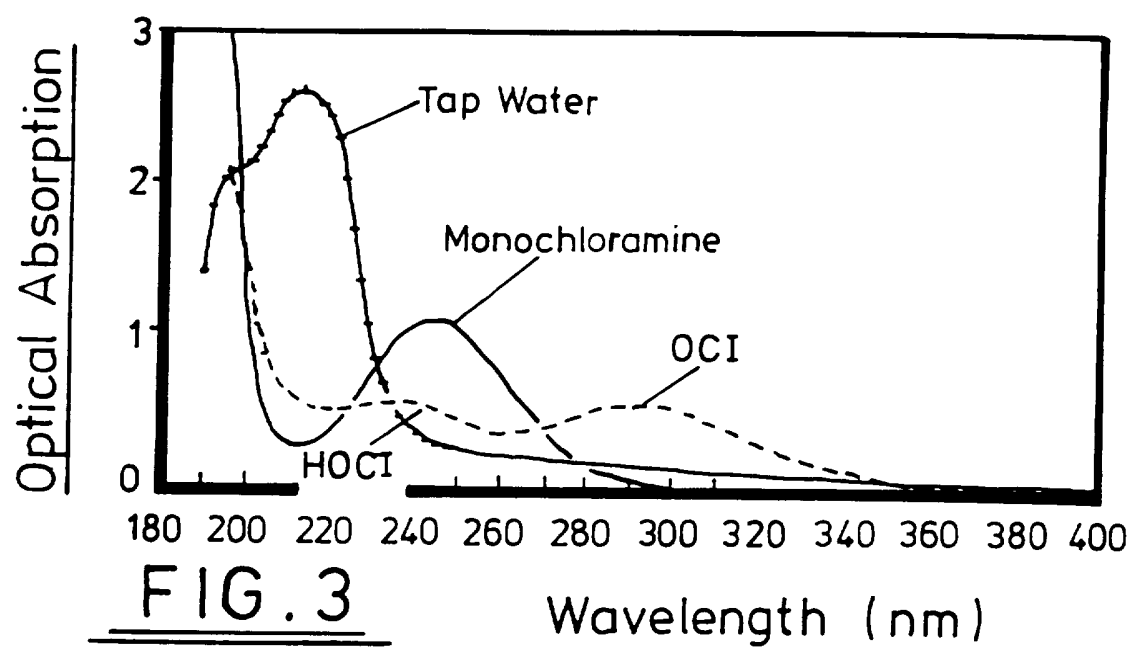
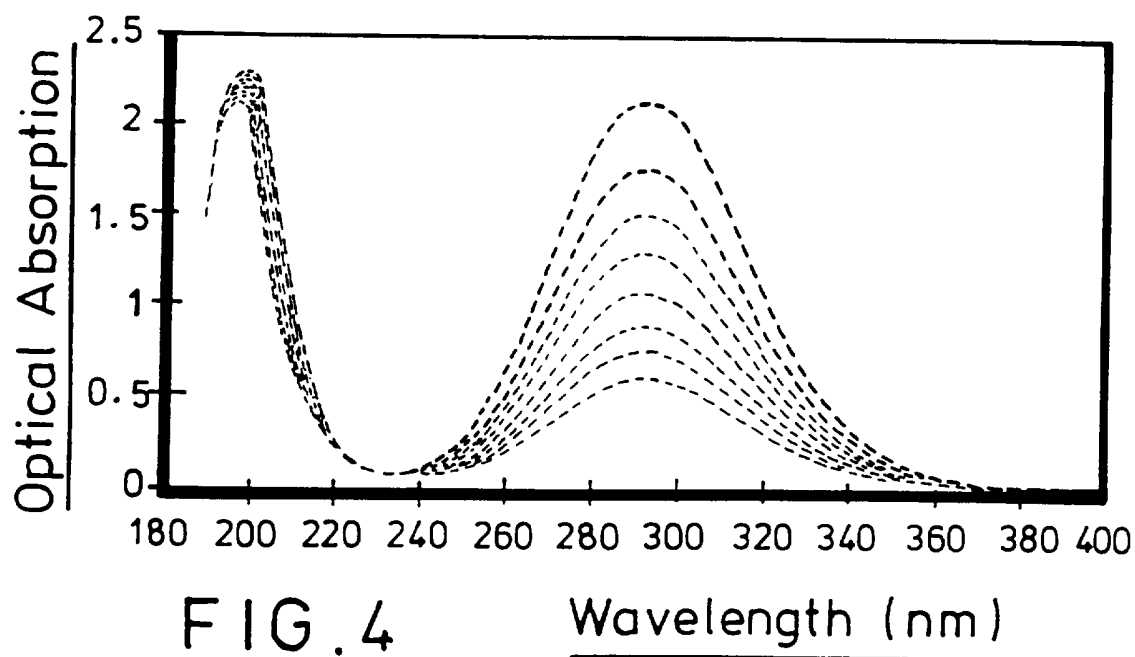
The above results indicate that the present invention produces good estimates of the concentration of HOCl and OCl⁻ using spectrum analysis techniques that can be readily applied using available software. In the worked example the matrix manipulations were performed using the well-known mathematics program "Mathcad". They are, however, simply programmed in any general purpose programming language such as Basic, Pascal or C, or in a spreadsheet. No specialised software is required for the spectral analysis, although such software is available, for example "Unscrambler" which is available from CAMO A/S, Olav Tryggvasonsgt. 24, N-7011, Trondheim, Norway.

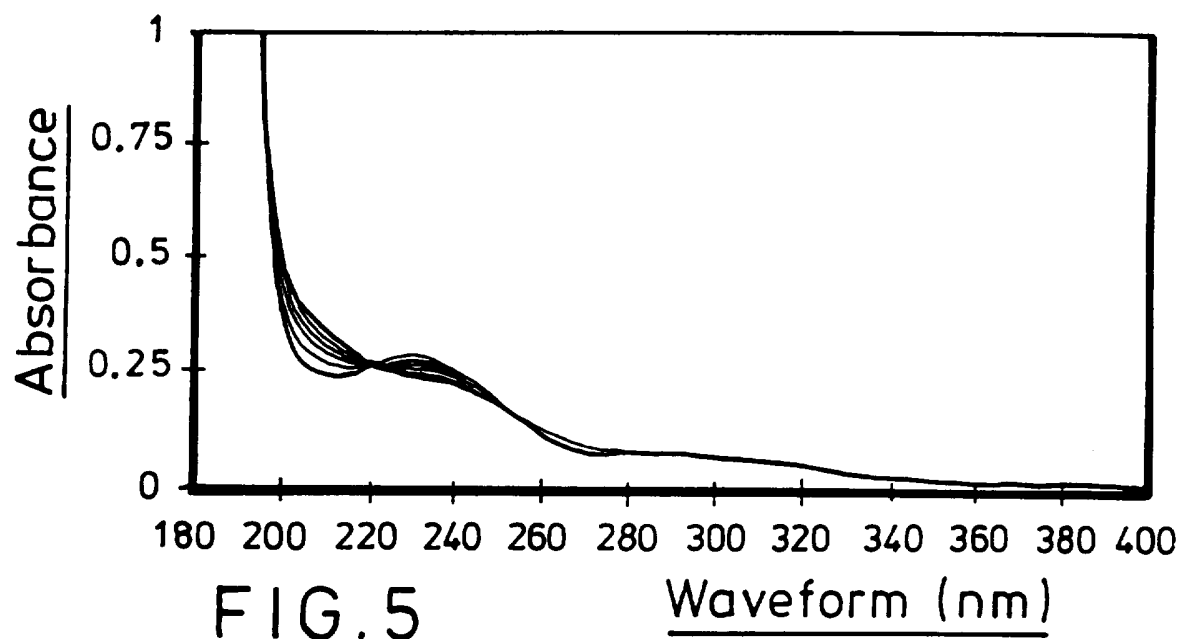
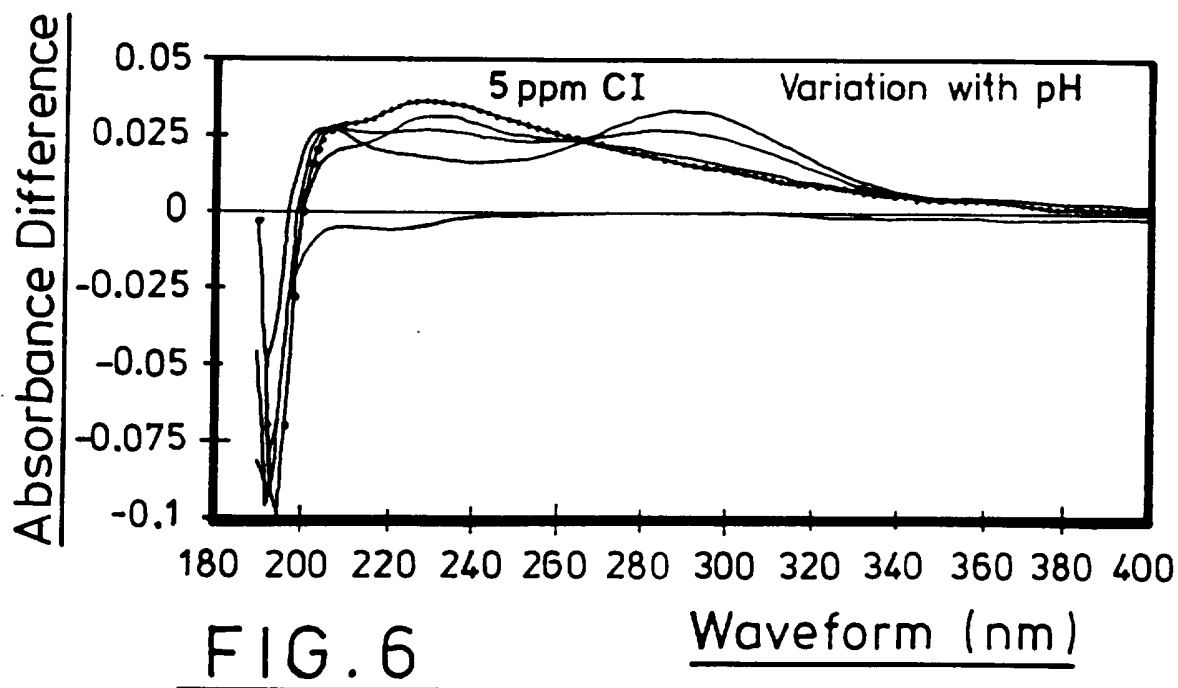
CLAIMS:

1. A method for determining the concentration of a target chemical species in a sample, wherein the absorbance of the sample is measured across a range of wavelengths to produce a first absorbance spectrum, the sample is exposed to conditions which modify the concentration of the target chemical species in the sample, the absorbance of the sample is re-measured across the said range of wavelengths to produce a second absorbance spectrum, and differences between the two spectra are analysed to quantify the concentration of the target chemical species in the unmodified sample.
2. A method according to claim 1, wherein the sample is exposed to radiation to photolytically modify the target species.
3. A method according to claim 2, wherein the sample is exposed to radiation in the presence of a photoconductor capable of generating reactive species.
4. A method according to claim 2 or 3, wherein the sample is irradiated with UV or visible light.
5. A method according to claim 2, 3 or 4, wherein the sample is irradiated by a continuously operating light source.
6. A method according to claim 2, 3 or 4, wherein the sample is irradiated by an intermittently operating light source.
7. A method according to claim 1, wherein an active species flux generated by a corona discharge is passed through the sample to modify the target chemical species concentration.

8. A method according to claim 7, wherein the corona discharge is generated by applying a voltage between a first electrode spaced from the sample and a second electrode immersed in the sample.
9. A method according to claim 8, wherein a grounded electrode is positioned between the first electrode and the sample to remove charged species.
10. An apparatus for determining the concentration of a target chemical species in a sample, comprising a spectrometer for making successive measurements of the absorbance of the sample across a range of wavelengths to produce at least two absorbance spectra, means for exposing the sample to conditions which modify the concentration of the target species in the sample, and means for comparing spectra generated before and after exposure of the sample to quantify the concentration of the target species.
11. An apparatus according to claim 10, wherein the exposing means comprises means for exposing the sample to radiation which photolytically modifies the target species concentration.
12. An apparatus according to claim 10, wherein the exposing means comprises means for generating a corona discharge so as to expose the sample to an active species flux which modifies the target chemical species concentration.
13. A method substantially as hereinbefore described with reference to the accompanying drawings.
14. An apparatus substantially as hereinbefore described with reference to the accompanying drawings.

1—8FIG. 1FIG. 2

2—8

3 — 8

4-8

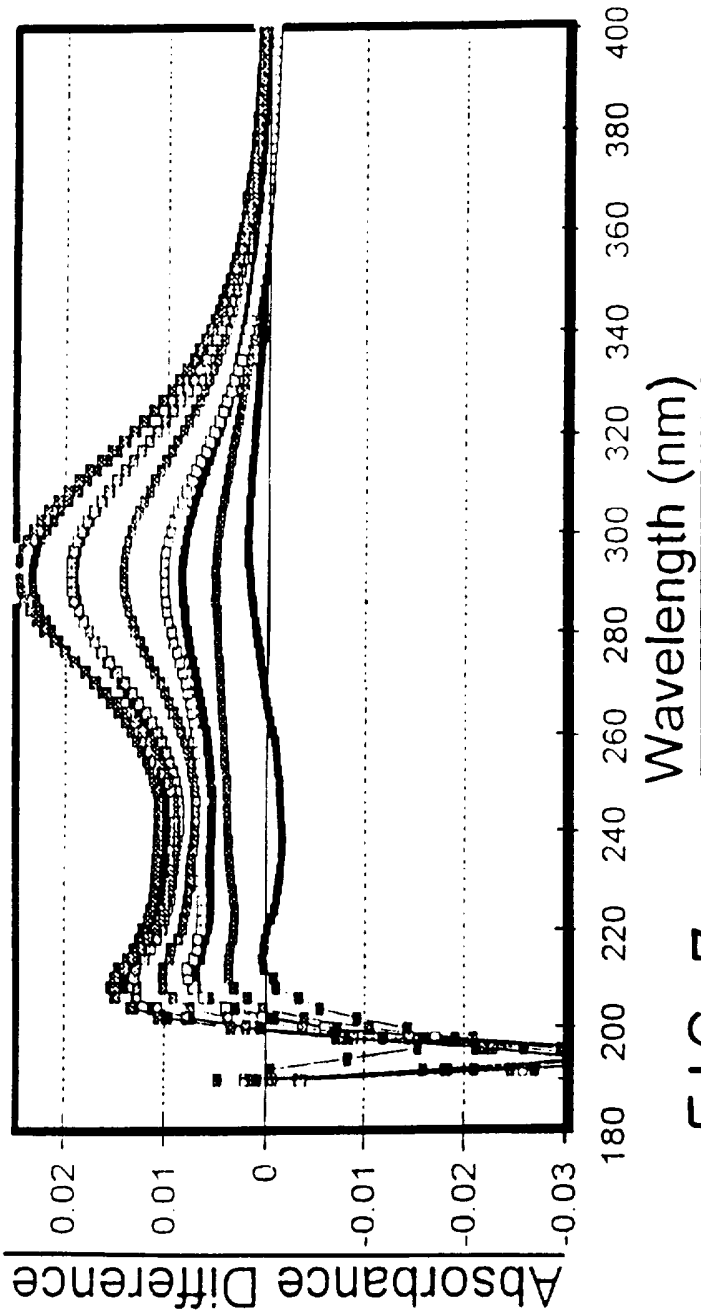


FIG. 7

5 — 8

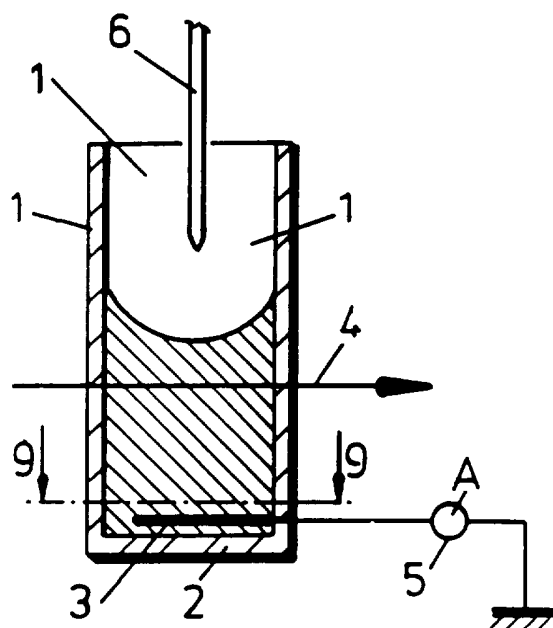


FIG. 8

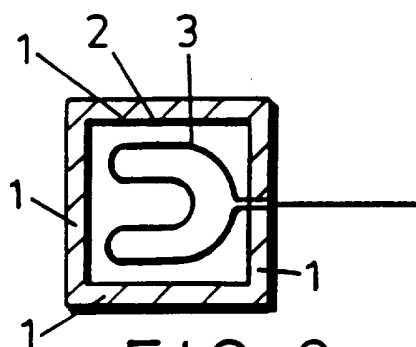
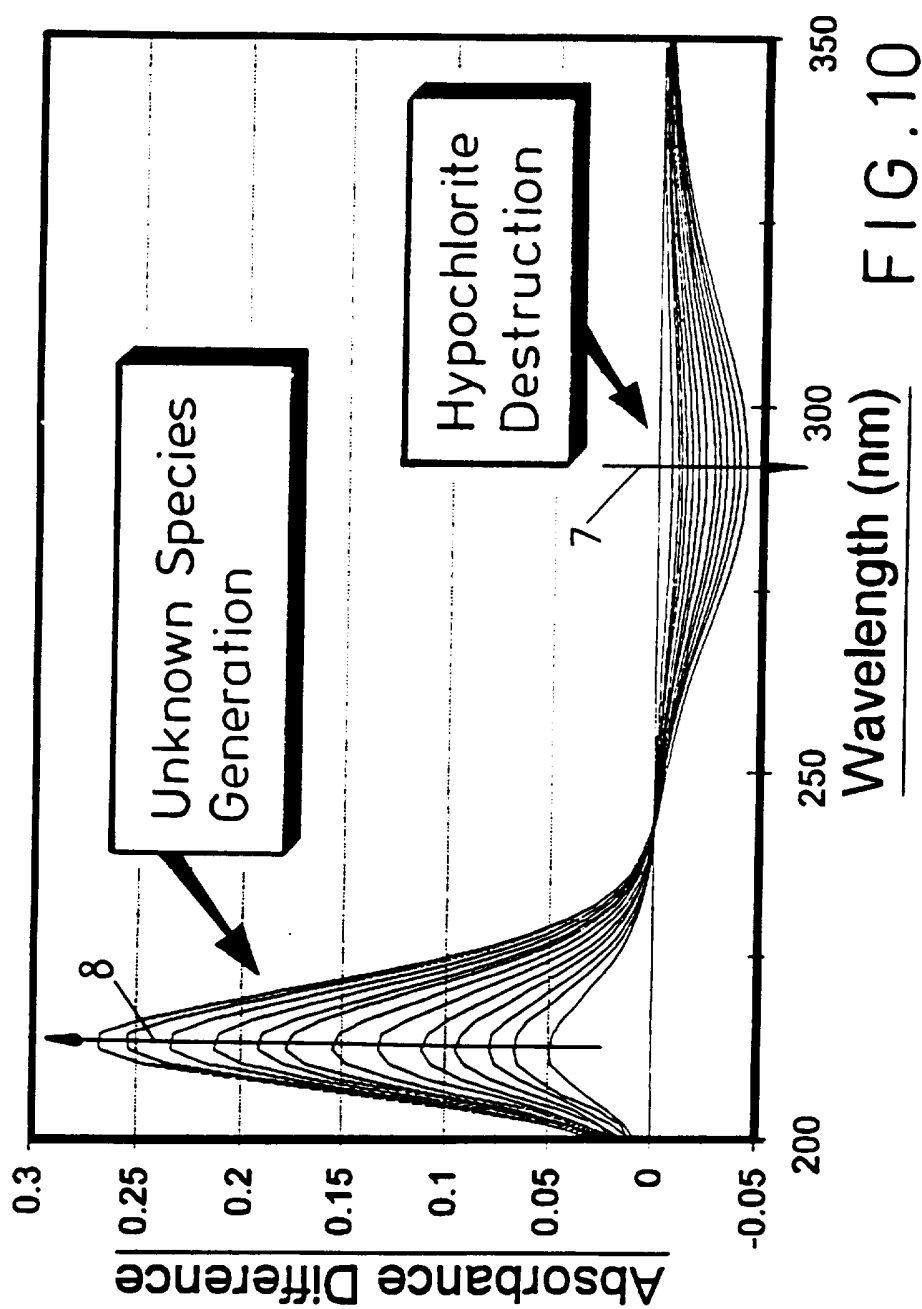
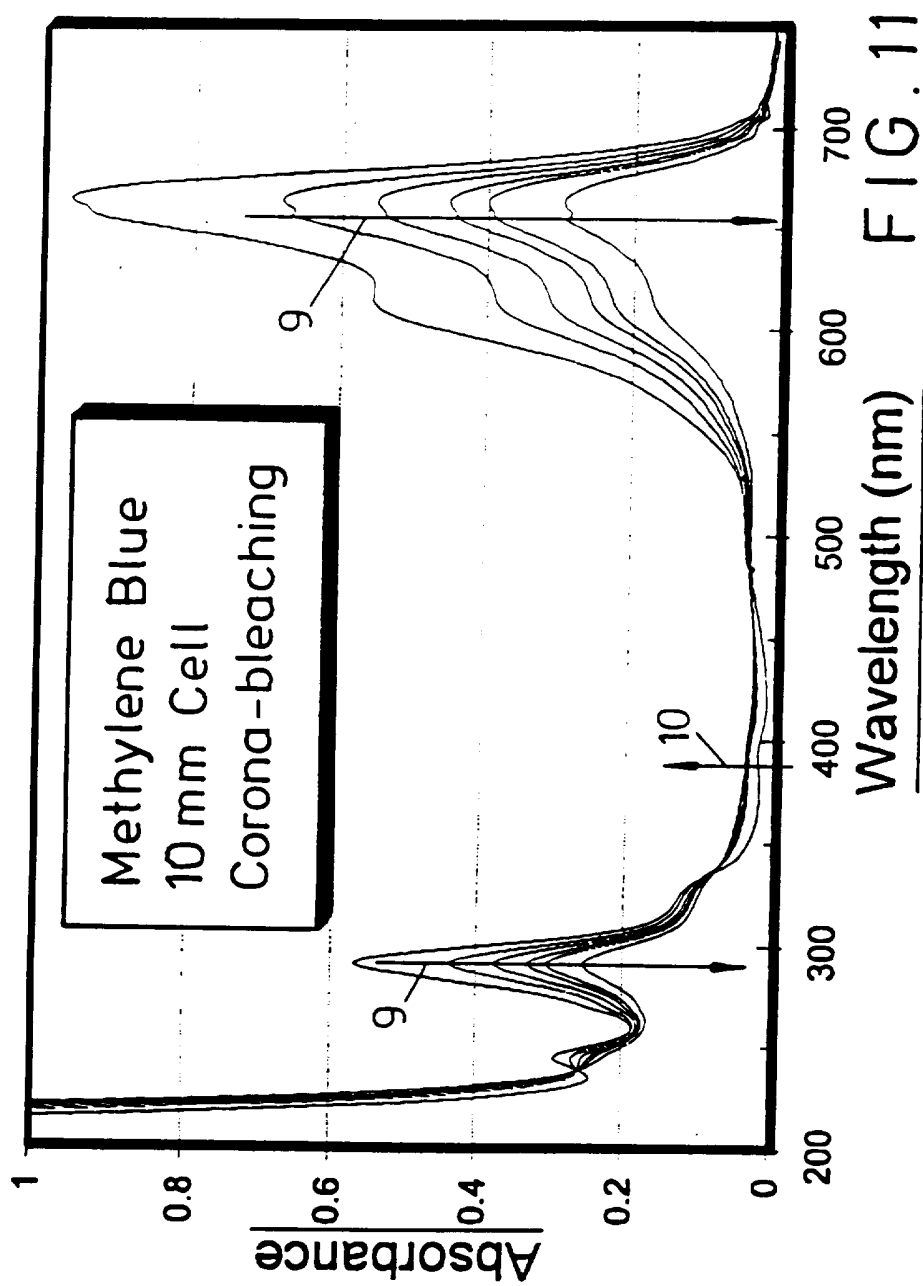
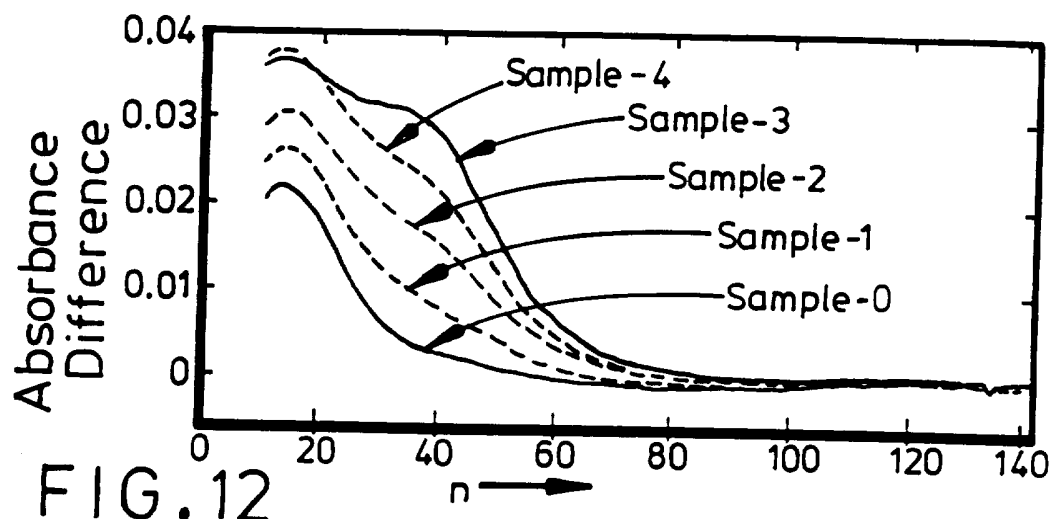
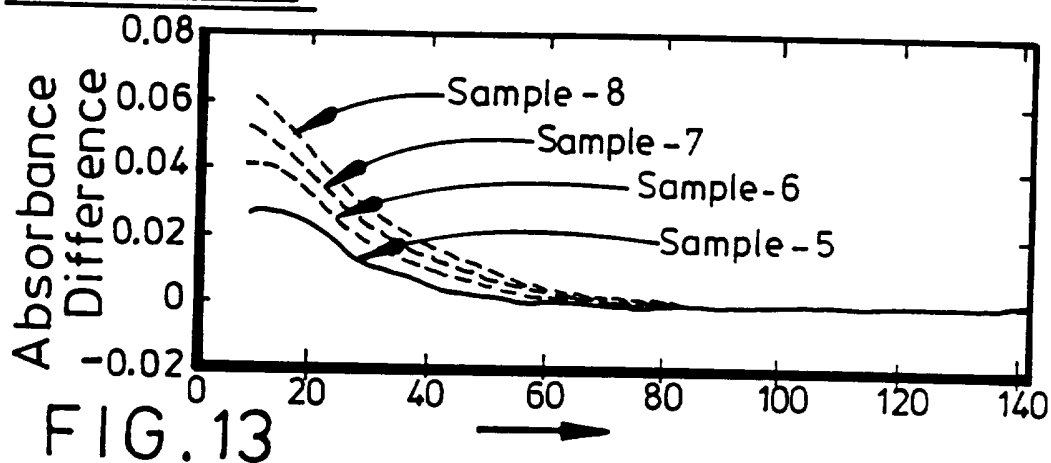
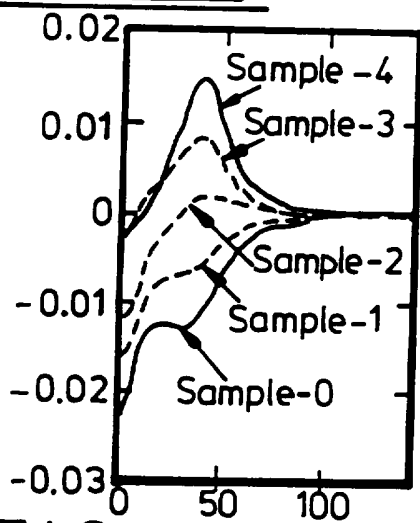
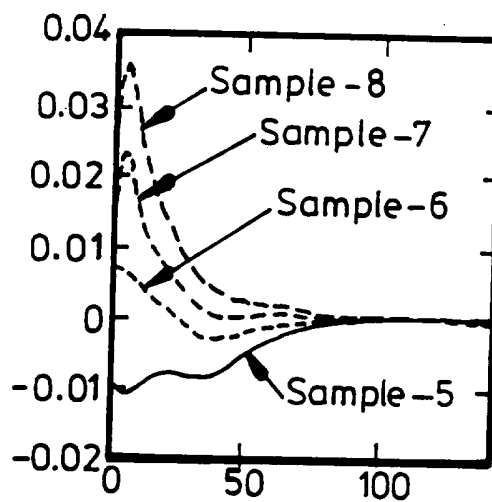


FIG. 9

6 — 8FIG. 10

7 — 8

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INTERNATIONAL SEARCH REPORT

Int ional Application No

PCT/GB 95/02862

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 G01N21/63 G01N21/17

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,5 298 428 (O'ROURKE PATRICK E ET AL) 29 March 1994 see the whole document ---	1,2,4,6, 7,10-12
X	WO,A,86 04673 (UNIV LEIDEN) 14 August 1986 ---	1,2,4,5, 10
A	see the whole document ---	11
X	PATENT ABSTRACTS OF JAPAN vol. 012 no. 095 (P-681), 29 March 1988 & JP,A,62 228145 (SHIMADZU CORP) 7 October 1987, see abstract ---	1,2,4,5, 7,10-12
A	US,A,4 023 905 (CHANCE BRITTON) 17 May 1977 see page 1; claims 1,3,6,15,16; figures -----	1,2,4,6, 10,11

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

29 March 1996

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 95/02862

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		EP-A- 0217819	15-04-87
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		US-A- 4801552	31-01-89
US-A-4023905	17-05-77	NONE	