Description

The present invention relates to a process for the continuous analysis of the chloride ions present in the first-fraction waters of a distillation column for hydrocarbons, in particular crude oils, or of residues of atmospheric distillation. This invention also relates to an analyser adapted to carry out said analysis process.

It is known that the chloride ions present in the first-fraction waters of a distillation column for hydrocarbons, in particular crude oils, generally originate from hydrolysable salts initially contained in the hydrocarbons, which are hydrolysed to form hydrochloric acid. This hydrochloric acid condenses in cooling circuits situated downstream of the head of the distillation column and is the cause of the corrosion observed in these circuits. These hydrolysable salts are mainly composed of $MgCl_2$ and of $CaCl_2$. To limit the quantity of these salts present in the hydrocarbons prior to distillation, it is customary to desalt these hydrocarbons using per se known means and to inject soda, after desalting, so as to effect the hydrolysis of these salts, replacing them with sodium chloride which is found in the distillation residues.

However, it is very difficult to adjust the amount of soda to be injected, since maintaining a high rate of soda injection is disadvantageous in view of the problems posed by high sodium contents in the subsequent treatment of the distillation residues, particularly those of the atmospheric and vacuum residues of a crude oil.

Moreover, to neutralise the residual hydrochloric acid present in the vapours escaping from the head of the distillation column, it is known to inject at least ammonia and/or a corrosion inhibitor. The rate at which ammonia is injected is linked to the pH value measured in the first-fraction waters, which is maintained in the vicinity of 6.

To adjust the rates of soda injection, or of corrosion inhibitor, it is necessary to be able to monitor continuously the chlorine content of the waters condensed in

the circuits of the distillation head, and that is with the shortest possible response time.

At present, in the case of the first-fraction waters of conventional atmospheric distillation, the analysis of the content of chloride ions is carried out discontinuously at relatively well spaced intervals of time, of the order of once per day. This analysis is typically an argentometry (or more rarely an ionometry), generally carried out on a sample in the Testing Laboratory of the Refinery, the result only reaching the operator 24 hours after the sample was taken. If the measurement shows that the content of chloride ions is higher than the desired value, the operator then varies the rate of soda injection and corrosion inhibitor; however, this action does not take effect immediately. If the time taken by analysis is added to the delay occurring between the variation of the rate of soda injection after the desalter and its effect on the first-fraction waters, it is observed that for nearly 30 hours conditions of serious corrosion can prevail in the head circuit of a conventional atmospheric distillation.

By measuring or estimating the rate of corrosion, the Applicant has verified that, when the content of chloride ions in the first-fraction waters exceeds 10 p.p.m., a sharp acceleration can be observed in the corrosion of the circuits in the distillation head. Therefore, the knowledge of this value (content of chloride ions) in real time is an important parameter for:

1. optimising the injection rates of soda and/or corrosion inhibitor;

2. increasing the service life of the head circuits and condensers;

3. recovering the atmospheric residue and the fuels, because of the problem posed by the presence of sodium in the fuels.

FR-A-2 342 496 discloses a process for the continuous analysis of the chloride ions present in the spent waters rejected by petrochemical installations, in accordance with which a sample is taken for analysis, the

sulphide ions are oxidised to sulphate ions and the chloride ions are measured by ionometry.

However, as far as the Applicant is aware, no process or apparatus exists which makes it possible to carry out satisfactorily the continuous analysis of the chloride ions present in the first-fraction waters of distillation. In fact, it has not been possible to solve two important technical problems:

- sulphur, in the form of S^{2-} and/or HS^{-} sulphide ions is also present in the waters whose chloride ion content is to be measured. These sulphide ions interfere with the measurement of chloride ions, by causing significant deviations or errors in the results; it will be recalled that the first-fraction waters of atmospheric distillations of crude oil may contain from 0 to 400 p.p.m. of S^{2-} and/or HS^{-} sulphide ions, depending on the nature of the crude oil;

- during the operation of distillation units it is possible for hydrocarbons to be entrained with the water, which causes gradual clogging of the sensitive portion of the electrode of the measuring cell, if the measurement is carried out by ionometry, and this measurement rapidly becomes unreliable.

It is the object of the present to obviate the above-mentioned disadvantages and, for this purpose, it relates, according to a first aspect, to a process for the continuous analysis of the content of chloride ions present in the first-fraction waters of a hydrocarbon distillation column (3), in accordance with which a sample flow of water to be analysed is taken from said first-fraction waters, the S^{2-} or HS^{-} sulphide ions in the samples of water taken are oxidised to sulphate ions, and the content of chloride ions present are measured by ionometry, said process being characterised by the following stages, prior to the measurement by ionometry:

- the hydrocarbons and other substances in suspension are eliminated from the samples of water taken from first-fraction waters;

- nitrogen is blown in so as to entrain the hydrogen sulphide and residual hydrocarbons;

- said sample is acidified.

Therefore, the process according to the invention makes it possible to obviate the disadvantages resulting from the presence of hydrocarbons and S^{2-} sulphide ions in said sample and, moreover, to avoid any deviation in the signal from the combined electrode when the pH is higher than 7. In fact, on the one hand, the sulphate ions do not interfere with this type of electrode and, on the other hand, the signal from this type of electrode is stable when the pH is maintained between 2 and 7.

For the person skilled in the art, the operation, comprising blowing nitrogen into said sample so as to entrain the hydrogen sulphide and the hydrocarbons, can be carried out upstream or downstream of the oxidation and acidification operations of said sample, since only the quantities of sulphates originating from the oxidation of a hydrogen sulphide vary.

In a first embodiment of the invention, the hydrocarbons of the sample of the first-fraction waters are eliminated by filtering through an activated carbon filter.

In a second embodiment, the sample of first-fraction waters can be introduced into a vessel comprising at least one hydrocarbon detector and at least one outlet duct provided with a valve or valves connected electrically to said detector, allowing the circulation of said sample towards a measuring cell and also the discharge of said sample when the hydrocarbons occupy an excessively large volume of said vessel.

To detect the presence of hydrocarbons in this sample it is possible to use capacitive sensors, for example a sensor sold under the name EFFECTOR by the firm IFM Electronic or any other suitable means.

The detection of hydrocarbons in said vessel has the advantage of mitigating operating problems in the regulation of the water level in the head flask of the distillation unit, which at certain times may result in an excessive and unforeseeable discharge of hydrocarbons

into the first-fraction water circuit of the distillation column at certain times.

The oxidation of S^{2-} and/or HS^- sulphide ions to sulphate ions is effected by injecting into said sample, from which the majority of the hydrocarbons have been removed, an oxidising solution whose oxidising capacity is sufficient, at the pH of said sample, to oxidise the S^{2-} and/or HS^- sulphide ions to sulphate ions but insufficient to transform the chloride ions to chlorate ions. Said injection of the oxidising solution is carried out at a pH value such that it enables the formation of free sulphur to be avoided, which would tend to clog the sensitive portion of the measuring electrode or electrodes.

Said oxidising capacity is dependent on the respective potentials, at the pH of said sample, of the oxidising-reducing equilibria of the ion pairs present.

Therefore, to oxidise the sulphide ions to sulphate ions, the oxidising solution can be chosen from the group comprising the BrO_3^- bromates, the $Cr_2O_7^{2-}$ bichromates, the MnO_4^- permanganates, the nitrates of alkaline, alkaline earth or other metals and any other anion which is oxidising for the sulphide ions but not oxidising for the chloride ions. The concentration of oxidising ions of said solution is between 0.1 M and 5 M and, preferably, between 0.5 M and 3 M.

In a first embodiment of the invention, since said oxidation has to be carried out at a pH value such that it enables the formation of free sulphur to be avoided, previously or simultaneously an alkaline agent is added so that the pH value is higher than 7, for example a soda solution having a concentration typically between 0.5 N and 2N. A preferred oxidising solution of said first embodiment of the invention comprises an aqueous solution of potassium permanganate and soda. In a second embodiment, it is necessary to add simultaneously or subsequently an acidifying agent to the sample so as to increase the oxidising capacity of the oxidising solution introduced. It will not constitute a departure from the scope of the invention if, in a single step, an agent is introduced into the sample which makes it possible simultaneously to increase the oxidising capacity of

the oxidising solution and to acidify said sample. A preferred oxidising solution of said second embodiment is a concentrated aqueous solution of sodium bromate ($NaBrO_3$).

The subsequent acidification of said sample to a pH of between 2 and 7, with a view to stabilising the electrode response, is effected to injecting a concentrated acid solution of 0.1 to 5N and, preferably, of 0.5 to 2N of at least one strong acid chosen from the group comprising sulphuric acid, nitric acid and the halogenated acids, with the exception of hydrochloric acid.

It should be noted that the rate of injection of the oxidising solution is between 0.001 and 0.5 times the rate of circulation of said sample in the analyser.

The invention also relates to an analyser for carrying out said process, which is characterised in that it comprises:

- a device for eliminating hydrocarbons, through which passes the first-fraction water sampled at the last first-fraction flask;

- a pneumatic or electric metering pump which takes the water from the outlet of the device for eliminating hydrocarbons;

- a reservoir provided at its bottom with a nitrogen supply intended to blow nitrogen into said sample and, at its top, with a membrane which is permeable to nitrogen and the volatile compounds, in particular to hydrogen sulphide H_2S and, optionally, to volatile residual hydrocarbons which are entrained by the nitrogen thus blown in;

- two devices for injecting, respectively, a first oxidising solution and a second acidifying solution, each comprising respectively a metering pump and a reservoir and containing said solution;

- a measuring cell comprising a closed electrolytic vessel provided with a specific combined electrode for measuring the concentration of chloride ions of said sample passing through said vessel, for example a combined electrode of CE 9417 B type sold by the firm ORION;

- and an associated electronic unit which is connected to said electrode and which gives the content of chloride ions present in the water, in any suitable form.

The specific combined electrode is adjusted in a manner known per se by means of standard solutions which are representative of the first-fraction water after treatment (oxidation and acidification) and containing ammonium chloride which has been added in different concentrations.

In a first embodiment of the device for eliminating hydrocarbons, it may comprise an activated carbon filter.

In a second embodiment, which is preferred insofar as it makes it possible to react more effectively to surges of hydrocarbons arriving in the waters collected in the last first-fraction flask, the eliminating device comprises a vessel provided with a hydrocarbon level detector, preferably a capacitive sensor of commercial type. Said vessel also comprises a first output circuit, which is disposed in the upper portion of said vessel, enabling the hydrocarbons to be eliminated, and a second circuit, which is disposed in its lower portion, conveying the sample of water without hydrocarbons towards the measuring cell. These circuits are advantageously provided with valve(s), the movement of which is controlled by said hydrocarbon level detector, for the purpose of cutting off the circulation of said sample towards the measuring cell when the hydrocarbons occupy an excessively large volume in the vessel and when there is a danger of entrainment, by said circuit, towards the hydrocarbon-measuring cell, which can alter the response of the combined electrode. The person skilled in the art could advantageously dispense with the valve disposed in the second output circuit of vessel and use the metering pump, disposed downstream, to cut off the flow of liquid coming from said vessel.

Any analyser has to have safety guarantees before it can be incorporated in an industrial installation; the analyser according to the invention also has to satisfy these requirements. It is characterised in that the assembly of its elements is enclosed in a safety housing which preferably has flame-proof characteristics when used in a refinery.

The invention will now be described with reference to the accompanying, non-restrictive drawings, in which:

Figure 1 respresents, by way of example, oil processing units up to the distillation thereof and the position of the chlorides analyser in the circuit for the first-fraction distillation vapours.

Figure 2 represents a diagram of the preferred embodiment of the analyser for chloride ions in accordance with the invention, and

Figure 3 represents the so-called POURBAIX oxido-reduction potential/pH graph of the zones with a presence of the species H_2S, HS^-, S^o, SO_4^{--}, Cl and ClO_4^-.

Referring now to Figure 1, a crude oil processing circuit comprises a desalter 1, in which the majority of the hydrolysable salts of the crude oil admitted through the duct 10 are eliminated, then a heating furnace 2, to which this crude oil is conveyed through a duct 11, a duct 12 enabling saline water to be removed, and an atmospheric distillation column 3 for the crude oil admitted through a duct 13.

The first-fraction distillation vapours escaping at the top of the distillation column 3 then pass, via a duct 14, through a first heat exchanger 4, in which their temperature is lowered to a sufficient extent to enable their heaviest hydrocarbons to condense; they are collected in a first first-fraction flask 5, whereas the water vapour from which the heaviest hydrocarbons have been removed is caused to pass through an air-cooling device 6 via a duct 15.

The heaviest hydrocarbons are collected at 22 at the bottom of the first first-fraction flask 5. The condensed water, discharged from the air-cooling device 6 through a duct 16, is recovered at the base of a second first-fraction flask 7 via a duct 17. The non-condensable gases escape from this latter flask through a duct 16' and the hydrocarbons through a duct 16". The duct 17 divides into two parallel circuits, a circuit 18a, into which the chlorides analyser 9 according to the invention is connected, and a circuit 18b in which continuous pH measurements are carried out by means of a pH meter 8; the two circuits reunite in a duct 19, the

condensed water being conveyed towards a downstream processing unit.

To limit corrosion throughout the first-fraction distillation circuit, an injection of ammonia NH_3 is carried out at 20, so as to maintain the pH value in the condensed water at 7 at a value of about 6. This injection is controlled by the measurement of the pH value given by the pH analyser 8. A first injection of corrosion inhibitor, at 21, and optionally a second injection, at 21', make it possible to limit corrosion by the first drops of dew which are formed in the air-cooling device 6 and which contain a very strong concentration of hydrochloric acid, of the order of several hundreds p.p.m. These injections are carried out in addition to an injection of soda effected at 22 in the duct 11, so as to combat corrosion effectively.

The continuous monitoring, by the analyser 9, of the chloride content of the condensed first-fraction waters makes it possible to act continuously, rapidly and accurately on the rates of injection at 21 and, optionally, 21' of corrosion inhibitor and, likewise, on the injection of soda at 22.

The chlorides analyser 9 according to the invention, illustrated in Figure 2,will now be described.

Said analyser 9 comprises a vessel 31, into which is fed the sample which enters through the duct 18a. It comprises two outlet ducts, one of which, 32, in its upper portion, enables the sample overladen with hydrocarbons to be discharged and the second of which, 33, in the lower portion of the vessel 31, facilitates the conveyance of the sample towards the rest of the analyser 9.

At its top, the vessel 31 is provided with a capacitive sensor 34 of commercial type (for example an EFFECTOR sensor), sensitive to hydrocarbons and connected to the detector 35 which, according to the signal coming from the sensor 34, acts by way of a relay 36 on the movement of the respective valves 37, disposed in the duct 32, and 37' disposed in the duct 33.

When the sensor 34 detects hydrocarbons in the bottom of the vessel 31, the valves 37 and 37' are actuated so as to shut off access to the rest of the analyser and to discharge the sample overladen with hydrocarbons through the outlet duct 32. The valves 37 and 37' return to their initial position when the sensor 34 no longer detects any hydrocarbons at the bottom of the vessel 31. The water then leaves through the duct 33 and passes through a pneumatic or electric metering pump 39. Downstream of the pump 39, the purified water is introduced into a reservoir 42. Nitrogen is blown into the bottom 43 of this reservoir at a predetermined rate so as to entrain the residual volatile hydrocarbons and hydrogen sulphide towards the porous membrane 44 disposed at the top of the reservoir 42. The oxidising solution and the acidifying solution, respectively stored in the reservoirs 40 and 40', are pumped by two metering pumps 41 and 41' respectively (or, optionally, a single double-headed metering pump), are then injected into the duct 45 which conveys the blown-in air leaving the reservoir 42. As will be explained below, the injection of the acidifying solution is effected after the injection of the oxidising solution.

The water thus treated is conveyed, via a duct 45, to the closed electrolytic vessel of the measuring cell 46, comprising a water-outlet orifice 47 which connects the duct 19, as shown in Figure 1, and provided with a specific combined electrode 48, for example of CE 9417 B type, sold by the firm ORION. Said electrode is connected to an associated electronic unit 49 which processes the electric signal generated by the measuring cell and restores it in the form of data which can be utilised directly (display of the chlorides content....) and/or optionally recorded. The chlorides content, which is continuously displayed, enables an operator, or a control system, to vary the rate of injection of corrosion inhibitor and that of soda.

Figure 3 represents a graph of the presence of the chlorinated species (Cl^-, ClO_4^-) and sulphurated species (S^o, H_2S, HS^-, S^{--} and SO_4^{--}) as a function of the oxido-reduction potential and of pH, in accordance with the so-called POURBAIX

represenation. The pH value, which varies from 0 to 14, is indicated on the x-axis and the potential, which varies from -1 to +2 volts, is indicated on the y-axis.

The curves indicated in solid line, which separate the presence zones, are the so-called molarity curves on which the species indicated is at a concentration of 1M. However, since its concentration varies exponentially as function of the potential along its curves, it may be assumed that the species is no longer present beyond said curve.

A first example of embodiment of applying the process according to the invention comprises, starting from a first-fraction water with a pH value of about 6 and reducing potential, represented symbolically by the point A in this graph, shifting as far the point B, with a pH value of about 9, by adding an alkaline agent, for example soda, then shifting it as far as C, with a pH value of about 9 and a potential higher than 0.4 volt, by adding an oxidising agent, for example potassium permanganate, then returning as far as D, with a pH value of about 5 and a potential higher than 1.1 volt, by adding an acidifying agent, for example nitric acid.

In fact, with the analyser as described above, the shift takes place directly from A to C by the addition of a solution which is simultaneously alkaline and oxidising; the person skilled in the art would be able to devise an analyser comprising three injection devices, the first of which serves to inject an alkaline agent, without thereby engaging in inventive activity and, therefore, without departing from the scope of the present invention.

The advantage of this shift in said POURBAIX graph lies mainly in avoiding the presence of the species of free sulphur (S^{o}) which, once formed, is stable and clogs the sensitive portion of the electrode which is produced from sintered silver in this type of combined electrode.

A second example of embodiment of applying the process according to the present invention comprises, starting from the same first-fraction water as in the preceding example, at pH = 6 and with reducing potential, represented by the same point A in this graph, shifting as far

as the point E with a potential of less than 0.2 volt, by adding an oxidising agent such as sodium bromate; then shifting as far as the point F, with a pH value of 2 and a potential higher than 0.4 volt, by adding an acidifying agent, for example nitric acid. The presence of nitric acid in the sample increases the oxidising capacity of the bromate ions, which makes it possible to prevent the formation of free sulphur while passing through the stabilisation zone of free sulphur (S^{o}).

Therefore, the process for continuous analysis and the analyser according to the invention make it possible to limit corrosion in the first-fraction condensers and circuits, thereby increasing their service life. They also make it possible to achieve substantial economies in the amounts of inhibitors injected into the first-fraction waters and to obviate the disadvantages of excessive injection of soda into the crude oil.

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CLAIMS:

1. A process for the continuous analysis of the content of chloride ions present in the first-fraction waters of a hydrocarbon distillation column (3), in accordance with which a sample flow of water to be analysed is taken from said first-fraction waters, the S^{2-} or HS^{-} sulphide ions in the samples of water taken are oxidised to sulphate ions, and the content of chloride ions present are measured by ionometry, said process being characterised by the following stages, prior to the measurement by ionometry:

- the hydrocarbons and other substances in suspension are eliminated from the samples of water taken from first-fraction waters;
- nitrogen is blown in so as to entrain the hydrogen sulphide and residual hydrocarbons;
- said sample is acidified.

2. A process according to claim 1, characterised in that the elimination of the hydrocarbons and the substances in suspension from said sample is effected by filtration through an activated carbon filter.

3. A process according to claim 1, characterised in that the elimination of the hydrocarbons from said sample is carried out by decanting in a vessel (31) comprising at least one hydrocarbon detector (34) and at least one outlet duct (32) provided with a valve or valves connected electrically to said detector (34), allowing the circulation of said sample towards a measuring cell and also the discharge of said sample when the hydrocarbons occupy an excessively large volume of said vessel (31).

4. A process according to any one of claims 1 to 3, characterised in that the S^{--} and/or HS^{-} sulphide ions are oxidised to sulphate ions by injecting into said sample an

oxidising solution whose oxidising capacity is sufficient to oxidise the sulphide ions to sulphate ions at the pH value of said sample but insufficient to oxidise the chloride ions to chlorate ions, said injection being carried out at a pH value such that it enables the formation of free sulphur to be avoided.

5. A process according to any one of claims 1 to 4, characterised in that the oxidising alkaline solution contains at least one salt chosen from the group comprising the BrO_3^- bromates, the $Cr_2O_7^{2-}$ chromates, the MnO_4^- permanganates, the NO_3^- nitrates of alkaline, alkaline earth or other metals and any other anion which is oxidising for the sulphide ions but not oxidising for the chloride ions, and optionally an alkaline agent.

6. A process according to claim 5, characterised in that the oxidising solution is a concentrated aqueous solution of 0.1M to 5M and 0.5M to 2M of potassium permanganate $KMnO_4$ and 0.5 to 2N of soda.

7. A process according to claim 5, characterised in that the oxidising solution is a concentrated aqueous solution of 0.1M to 5M and 0.5M to 2M of sodium bromate $NABrO_3$.

8. A process according to any one of claims 1 to 7, characterised in that said sample is subsequently acidified by injecting a concentrated acidifying solution of 0.1N to 5N and 0.5N to 2N of at least one strong acid chosen from the group comprising sulphuric acid, nitric acid and the halogenated acids, with the exception of hydrochloric acid.

9. A process according to any one of claims 1 to 8, characterised in that the rate of injection of the oxidising solution is between 0.001 and 0.5 times the rate of circulation of said sample in the analyser.

10. An analyser for carrying out the process according to any one of the preceding claims, characterised in that it comprises:

- a device (31) for eliminating hydrocarbons, through which passes the first-fraction water sampled at the last first-fraction flask;

- a pneumatic or electric metering pump (39) which takes the water from the outlet of the device (31) for eliminating hydrocarbons;

- a reservoir (42) provided at its bottom (43) with a nitrogen supply intended to blow nitrogen into said sample and, at its top, with a membrane (44) which is permeable to nitrogen and the volatile compounds which are entrained by the nitrogen thus blown in;

- two devices for injecting, respectively, a first oxidising solution and a second acidifying solution into the circulation duct (45), each comprising respectively a metering pump (41 and 41') and a reservoir (40 and 40') containing said solution;

- a measuring cell (46) comprising a closed electrolytic vessel (47) provided with a specific combined electrode (48) for measuring the concentration of chloride ions of said sample passing through said cell;

- and an associated electronic unit (49) which is connected to said combined electrode (48) and which processes the electric signal generated by said combined electrode and restores it in the form of data which can be utilised and/or optionally recorded.

11. An analyser according to claim 10, characterised in that the device for eliminating hydrocarbons is an activated carbon filter.

12. An analyser according to claim 10, characterised in that the device (31) for eliminating hydrocarbons is composed of a vessel provided with a hydrocarbon level detector (34) comprising:

- a first output circuit (32) provided with a first valve (37) controlled by the detector (34) enabling the sample to be eliminated when the hydrocarbons occupy an excessively large volume;

- and a second circuit (33) in the lower portion conveying the sample of water without hydrocarbons towards the measuring cell (46), said second circuit (33) being provided with a second valve (37'), the movement of which is controlled simultaneously by said detector (34) for the

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purpose of cutting off the circulation of said sample towards said cell (46) when the hydrocarbons occupy an excessively large volume.

13. An analyser according to any one of claims 10 to 12, characterised in that the assembly of the elements of the analyser (9) is enclosed in a safety housing which complies with the safety standards of the user industry.