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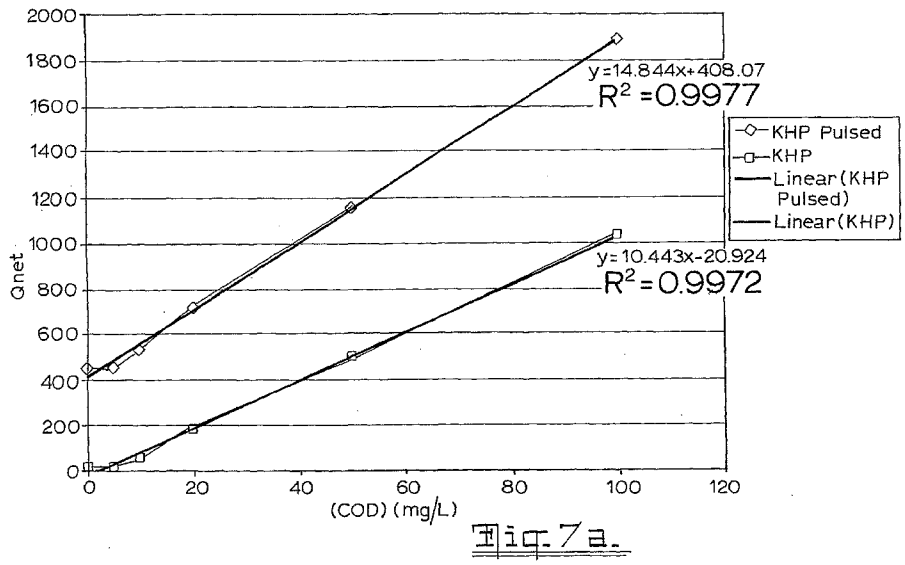


Fig. 7a.

(57) Abstract: A method of determining chemical oxygen demand in water samples containing chloride ions by a photoelectrochemical method in which the photo electrode is activated by light pulses and the pulse parameters and the light source intensity are set to favour the oxidation of organic species in the water sample and to suppress any oxidation from the chloride ions present in the sample. The method controls the duration of the pulse, the gap between pulses and the light intensity.

WO 2009/049366 A1

WATER ANALYSIS

Field of the Invention

This invention relates to a method for the determination of oxygen demand of water using photoelectrochemical cells. In particular, the invention relates to a photoelectrochemical method of determining chemical oxygen demand in water samples having high chloride content, such as sea water.

Background to the Invention

Nearly all domestic and industrial wastewater effluents contain organic compounds, which can cause detrimental oxygen depletion (or demand) in waterways into which the effluents are released. This demand is due largely to the oxidative biodegradation of organic compounds by naturally occurring microorganisms, which utilize the organic material as a food source. In this process, the organic carbon is oxidised to carbon dioxide using dissolved oxygen.

The standard aggregate measurements of oxygen demand in water are biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD). BOD_5 involves the use of heterotrophic microorganisms to oxidise organic material and thus estimate oxygen demand. COD uses strong chemical oxidising agents such as dichromate or permanganate to oxidise organic material. The BOD_5 analysis is carried out over five days and oxygen demand is determined by titration or with an oxygen probe. COD is determined by the measurement of dichromate or permanganate depletion by titration or spectrophotometry.

However, the oxidising ability of dichromate is so high that chloride ions present in a sample are easily oxidized to chlorine. Experiments have shown that the degree of oxidation of chloride is not predictable under practical conditions. This unpredictability causes the determination of small amounts of organic matter in the presence of high chloride concentrations (such as is found in estuarine waters) to be unreliable. To suppress this side-reaction, mercury sulphate ($HgSO_4$) may be used for samples containing chloride up to 2000 mg L^{-1}, above which COD cannot be accurately measured. Both dichromate and mercury are hazardous to environment and it is not desirable that routine methods utilize significant amounts of such substances. Seawater concentrations of chloride can be as high as 21,000 mg L^{-1}. Even with significant dilutions of sample to bring the chloride concentration

within range, the dichromate method will struggle with sensitivity.

Seawater is typically used in cooling towers to cool the condenser and for a number of other applications. However, the monitoring of seawater is required to avoid potential environmental concerns related to its usage and discharge. The ability to measure COD in seawater is an enormous industry application that is yet to be catered for.

Application WO2004/088305 discloses a photoelectrochemical method for detecting chemical oxygen demand as a measure of water quality using a titanium dioxide nanoparticulate semiconductor electrode. Titanium(IV) oxide (TiO_2) has been extensively used for the photooxidation of organic compounds. TiO_2 is non-photocorrosive, non-toxic, inexpensive, relatively easily synthesised in its highly active catalytic nanoparticulate form, and is highly efficient in photooxidative degradation of organic compounds.

A problem encountered in conducting assays using this method is dealing with interference from competing oxidisable chemical species other than organic carbon. Filtration of samples reduces interference from many species but the presence of chloride still remains a significant interference that must be dealt with. Chloride is commonly oxidized by photocatalysis to chlorine according to the following equation:

$$2Cl^- + h\nu \rightarrow Cl_2 + 2e^- \qquad \text{Equation 1}$$

The produced chlorine can be readily converted into hypochlorite under UV illumination (Equation 2) and production of other possible products including ClO_2^-, ClO_3^- and ClO_4^- may also occur. However, the photoxidation kinetics of Cl^- has proven to be slow.

$$Cl_2 + H_2O \xrightarrow{h\nu} HClO + HCl \qquad \text{Equation 2}$$

The standard COD detection method deals with chloride interference by chemically removing the chloride ions. The principle is to add a chemical that can form insoluble compounds with Cl^-, which can then be separated from the sample solution (see following reactions):

$$2Hg^{+}\,(aq) + 2Cl^{-}\,(aq) \rightarrow Hg_2Cl_2\downarrow(solid), \qquad K_{sp}=1.3\times10^{-18}$$

$$Ag^{+}\,(aq) + Cl^{-}\,(aq) \rightarrow AgCl\downarrow(solid), \qquad K_{sp}=1.0\times10^{-10}$$

The method involves the use of expensive and toxic chemicals and requiring separation. For online applications, the system will need a sophisticated component to achieve *in situ* separation of precipitated AgCl or Hg_2Cl_2, which, on one hand will significantly undermine the accuracy and reliability of the system, and on the other hand will increase both the capital and operational costs.

For both Industry and environmental management, there is considerable need to be able to measure the levels of organic content (or contamination) in water containing low to high levels of chloride (e.g. in sea water). Chloride is a problem for organic content measurement in aqueous samples as current methods of analysis can't easily distinguish between organic and chloride content and hence it creates an erroneous measurement.

Historically, the US EPA has approved a method of dichromate digestion for organic contamination measurement, specifically for chemical oxygen demand (COD). This requires the addition of mercury or silver salts to precipitate chloride containing compounds from the aqueous solution prior to analysis. Often this is accompanied by sample dilution in order to fully precipitate the chloride ions from the solution and to provide a solution capable of being analysed spectrophotometrically or by potentiometric titration. Thus low level organic content is not easily measured with any accuracy. This method also produces toxic salts that require specific materials handling procedures for disposal.

Another established method is total organic carbon (TOC) measurement. Difficulties in the presence of chloride also exist for TOC in that for persulphate based oxidation, false positives arise due to the inability to distinguish between chloride ions and the organic compounds in the solution. For high temperature oxidation based TOC, the chloride salts calcine and can cause instrumental errors through degraded operating performance, thus leading to high maintenance requirements for the technique and an inability to conduct regular on-line measurements.

WO2007/016740 discloses an improvement in the photoelectrochemical method for detecting chemical oxygen, previously described in WO2004/088305, which deals with the interference by chloride. In water samples containing chloride ions above 0.5mM concentration in which the samples are diluted, and a known quantity of an organic substance is added to the diluted sample which is then subjected to an assay by a photoelectrochemical method using a titanium dioxide photoactive nanoparticulate semiconductor electrode, the chemical oxygen demand is measured in the same manner as disclosed in WO2004/088305, except that a known concentration of organic solution is used to obtain the blank for calculation of the analyte charge.

PCT/AU2007/000735 discloses a similar method for dealing with difficult to oxidise organic compounds.

With either of these organic addition methods, the analytical signal is generated in exactly the same way as for the photoelectrochemical method disclosed in WO2004/088305.

However, this addition method requires some level of prior knowledge of the range of chloride, or of the difficult to oxidise organic compound concentration, and the organic contents in the samples in order to determine how much organic material to add in order to ensure total suppression of the chloride interference, and thus an accurate COD measurement.

While in many cases, this is not a serious issue, in environments such as sea water, where the chloride content is high, high levels of organic addition and sample dilution may be required and this can have an impact on the sensitivity that is then achievable.

It is an object of this invention to provide a simpler method of dealing with interference from chloride compounds, particularly in seawater.

Brief Description of the Invention

To this end, the present invention provides a method of determining chemical oxygen demand in water samples containing chloride ions by a photoelectrochemical method in which the photo electrode is activated by light pulses and the pulse parameters and the light source intensity are set to favour oxidation of the organic species in the water sample and to suppress any

oxidation signal from the chloride ions present in the sample.

By balancing the light intensity and light pulse parameters, the speed of organic oxidation and sensitivity may be optimised, without triggering chloride oxidation and the ensuing photocatalytic cyclic chloride oxidation reaction.

As examples of the effectiveness of this novel technique, the measurement of 1 mg/L organic content is achievable in seawater. The effectiveness of the method of this invention means that potassium Chloride may be used as the supporting electrolyte without compromising the effectiveness of the measurements.

Upon absorption of light by the TiO_2 photocatalyst, electrons in the valence band are promoted to the conduction band (e_{cb}^-) and holes are left in the valence band (h_{vb}^+). The photohole is a very powerful oxidizing agent (+3.1 V) that will readily lead to the seizure of an electron from a species adsorbed to the solid semi-conductor. Thermodynamically, both organic compounds and water can be oxidized by the photoholes or surface trapped photoholes but usually organic compounds are more favorably oxidized, which leads to the mineralization of a wide range of organic compounds. This is described in application WO2004/088305 the contents of which are incorporated herein by reference.

Owing to the strong oxidation power of photoholes, photocatalytic oxidation of organic compounds at TiO_2 electrode leads to stoichiometric oxidation (degradation) of organic compounds as follows:

$$C_yH_mO_jN_kX_q+(2y-j)H_2O \rightarrow yCO_2+qX^-+kNH_3+(4y-2j+m-3k)H^+ +(4y-2j+m-3k-q)e^-$$

where N and X represents a nitrogen and a halogen atom respectively. The numbers of carbon, hydrogen, oxygen, nitrogen and halogen atoms in the organic compound are represented by *y*, *m*, *j*, *k* and *q*.

In order to minimize the degradation time and maximize the degradation efficiency, the photoelectrochemical catalytic degradation of organic matter is preferably carried out in a thin layer photoelectrochemical cell. This process is analogous to bulk electrolysis in which all of the analytes are electrolysed and Faraday's Law can be used to quantify the concentration by measuring the charge passed if the charge/current produced is originated from photoelectrochemical degradation of organic matter. That is:

$$Q = \int idt = nFVC$$

where *n* refers to the number of electrons transferred during the

photoelectrocatalytic degradation, which equals *4y-2j+m-3k-q*, *i* is the photocurrent from the oxidation of organic compounds. *F* is the Faraday constant, while *V* and *C* are the sample volume and the concentration of organic compound respectively.

The measured charge, Q, is a direct measure of the total amount of electrons transferred that result from the complete degradation of all compounds in the sample. Since one oxygen molecule is equivalent to 4 electrons transferred, the measured Q value can be easily converted into an equivalent O_2 concentration (or oxygen demand). The equivalent COD value can therefore be represented as:

$$COD\ (mg\ /\ L\ of\ O_2) = \frac{Q}{4FV} \times 32000$$

This COD equation can be used to quantify the COD value of a sample since the charge, Q, can be obtained experimentally and for a given photoelectrochemical cell, the volume, *V*, is a known constant.

The net charge by pulsing is calculated according to the Equation 3, where the charge of the last pulse, nominated as Q_{blank} is subtracted from each pulse and from this the sum of all pulses results in Q_{net} (see Figure 4).

- $Q_{net} = \sum(QPulseTotal - QBlank)$ (for all n pulses) (pulse equation)

The total net charge (sum of all pulses) for each concentration increases with increasing concentration to show a linear relationship for the pulsing technique . However the net charge obtained does not equate to the relationship between Faraday's law and organic concentration and is in fact lower. This suggests that electrons are not all (captured) gathered at low LED intensity.

In another aspect, the present invention provides a photoelectrochemical assay apparatus to determine oxygen demand of a water sample which consists of

a) a flow through measuring cell

b) a photoactive working electrode and a counter electrode disposed in said cell,

c) a UV light source, adapted to illuminate the photoactive working electrode in pulses

d) a control means to control the pulsed illumination of the working electrode, the applied potential and the signal measurement

e) a current measuring means to measure the photocurrent at the working and counter electrodes

f) an analysis means to derive a measure of oxygen demand from the measurements made by the photocurrent measuring means.

The control means sets the duration of the pulse, the gap between pulses and the light intensity. Preferably the pulse duration is from 0.01 to 5 seconds and the interval between pulses is at least 1 second.

Preferably a reference electrode is also located in the measuring cell and the working electrode is a nanoparticulate semiconductor electrode, preferably titanium dioxide. The flow rate is adjusted to optimise the sensitivity of the measurements. This cell design is based on that disclosed in application WO2004/088305 with a means to store the organic/electrolyte solution. The sample collection device may include a filter to remove any large particulates, or precipitated substances, that may interfere with the operation of the cell.

The method of this invention may be combined with the organic addition method disclosed in WO2007/016740, the contents of which are incorporated herein by reference. The combination is useful when chloride content is high.

The limitation of the organic addition method, however, is that some prior knowledge of the level of chloride or difficult to oxidise organics is required before the appropriate level of catalytic organics may be added.

The method embodied by this invention avoids this constraint by the use of pulsed light. By this method, the reaction of the chloride is discriminated against by the pulsed waveform, and the COD may be determined in high saline matrices.

Description of the Drawings

Preferred embodiments of the invention will be described with reference to the drawings in which:

Figure 1 is a graph illustrating varying LED intensities applied to a 1 : 50 dilution of a seawater sample resulting in a chloride content of 425 mg/L Cl^-;

Figure 2 illustrates calibration, showing the linear relationship between concentration as COD and charge response for standards ranging from 0 – 50 mg/L COD in a background of 0 - 150 mg/L Cl^- in the cell **a.** Pulsing technique, **b.**

standard PeCOD analysis where there is a clear effect by a significant presence of chloride;

Figure 3 illustrates the signal response for saline and non-saline Potassium Hydrogen Phthalate (KHP) standards over a concentration range of perchlorate electrolyte. a.) non-saline, b.) saline (425 mg/L chloride);

Figure 4 illustrates the calibration over a concentration range for saline (s = 35) and non-saline (S=0) sample; a.) KHP, b.) Glucose. Analyses were performed using 1:50 dilution and a pulse of 0.5 sec on and 5 sec off;

Figure 5 illustrates the influence of chloride presence on the analytical signal. Figure 5a shows the normal response for KHP in the presence (upper trace) and absence (lower trace) of 1000 mg/L chloride with direct light;

Figure 5b shows the response for 5a above (chloride present) with a pulsed regime;

Figure 6 illustrates the calibration over a concentration range for saline samples at various dilutions, with and without organic addition. Analyses were performed using a pulse of 0.1 sec on and 1 sec off;

Figure 7 illustrates the calibration over a concentration range for saline and non-saline sample; a.) comparing pulsed and non-pulsed methods, b.) Comparison of saline and non-saline samples for the pulsed analysis method. Analyses were performed using a pulse of 0.1 sec on and 1 sec off;

Figure 8 provides comparative data for COD (PeCOD™) and BODsugar refinery samples in salt water;

Figure 9.illustrates the relationship between PeCOD™ COD and BOD values.

Detailed Description of the Invention

PeCOD™ is the trademark of the applicant that is used to designate the water analysers made in accordance with WO2004/088305.

By changing the amount of light energy reaching the working TiO_2 electrode, the rate of oxidation of Cl^- can be manipulated as seen in Figure 1. Figure 1 shows that when a dilution of 1 to 50 of seawater is made, resulting in a chloride content of 425 mg/L Cl^-, and when the applied UV light level applied is low, the onset of chloride oxidation is delayed and a window of opportunity exists where organics can be oxidised prior to the oxidation of chloride. At a LED intensity of 20% it was

observed that 5 mg/L of organic could be easily observed above the chloride content.

The oxidation times required for KHP and Glucose in saline and freshwater matrixes was observed. As predicted the oxidation time in the presence of chloride was higher in most incidences. Confirming that chloride slows the oxidation process. There were some differences observed in the oxidation times for glucose and KHP. Generally the oxidation of a larger molecule such as KHP would typically be expected to take longer. However, it was almost the opposite when chloride is present. Glucose appeared to take longer, and produced a different and broader profile compared to KHP. This anomaly may be explained if we consider KHP to be the larger molecule, with a better ability to compete for sites with chloride as opposed to glucose. Hence glucose oxidation will take slightly longer in the presence of chloride

Experiments were performed on the PeCOD™ L100 COD analyser to validate the potential of the pulsing technique for chloride analysis.

The sensors were made according to the colloidal method disclosed in WO2004/088305 and Australian application 2007906272.

Table 1 – Characteristics of sensor

Colloid pH	3.81
Pre-concentration temperature (°C)	90 for 3 hours
Sonication time approx. (hours)	8
Iterm (standard method)	34 (15% LED)
Burn in required for activation	30 min

It is believed the off-time can influence the state of the chloride reaction. The full photoxidation of chloride becomes a cyclic reaction, forming a number of intermediates, as seen in equations 1 & 2. The lower light intensity reduces the energy provided to the reaction and the ability of the electrons to reach the conduction band. This prevents the full cyclic reaction of chloride. However, this is not to say that electrons are not being excited to a higher state and it is therefore inferred that a sufficient off-time is required to allow electrons and intermediates to return to ground state.

However, lower light intensity does raise other issues, including sensitivity (signal to noise response), increased run time (due to both the slower oxidation of organic), and an increase in the number of pulses required (due to shorter pulse times).

The pulsing technique was shown to be a viable method for handling chloride levels up to 150 mg/L in the cell without any difficulties (Figure 2a). The same experiment was performed using the standard PeCOD algorithm without pulsing. This experiment revealed that levels of chloride up to 150 mg/L in the cell have a substantial effect on the accumulated net charge (Figure 2b). This reduced recovery is due to integration errors which present results that are not analytically useful.

The length of pulses for which the LED was on was studied in order to provide a universal method for determining COD in both chloride and non-chloride containing matrices. The influence of pulse time is addressed below.

KCl is a common electrolyte used in electrochemistry, and subsequently the potential for its use as a replacement electrolyte to the currently used $NaNO_3$ was investigated. KCl is a good electrolyte (due to its enhanced ionic mobility) and potentially it can provide a high background of chloride that would mask any chloride present in a sample. Preliminary experiments investigated the ability to detect low COD concentrations in a 1M KCl electrolyte. Figure 4a shows that 10 ppm of COD could be detected in KCl and hence a high chloride background using the pulsing technique. However, further tests showed the reproducibility to be poor and the ability of the signal to return to baseline could not be repeatedly achieved. The linearity and response over a concentration range was investigated for both saline and non-saline standards with Potassium Hydrogen Phthalate (KHP) in the range 0-300 mg/L. The responses are shown in Figure 3.

Sodium perchlorate is a preferred electrolyte that for the PeCOD™ instrument. It can achieve excellent linearity, use lower concentrations and is also hygroscopic. For this reason it was also investigated for its use in the application of analysis of COD in a chloride matrix.

The linearity and response over a concentration range was investigated for both saline and non-saline standards in the perchlorate electrolyte. The responses are shown in Figure 3, where the organic used was KHP. Interestingly the signal

shape and response between saline and non-saline samples were quite similar as opposed to previous results with nitrate which exhibited different kinetic properties between the two matrices. It is believed that the perchlorate being more conductive than its counterpart in nitrate, possess enhanced ion mobility allowing increased transfer of ions towards the titanium dioxide surface.

The results over the concentration range were tested for linearity for both KHP and glucose. The results obtained showed minimal differences between the gradients for a non-saline and saline sample (Figure 4).

Improved signal-to-noise and shorter pulses were investigated to increase sensitivity, accuracy and sample throughput time. It is proposed that the LED current is proportional to power and hence proportional to the terminal current. By increasing the power (measured in Joule/sec) and by keeping the energy the same (i.e. decreasing the duration of time that the LE was in the on state), the migration of chloride ions can be manipulated. By increasing the current applied, but at the same time decreasing the on time of oxidation in pulse mode, a higher LED current is permitted which results in more rapid oxidation and increased diffusion, in addition to increased sensitivity and signal-to-noise ratio.

The initial pulsing parameters in pulsing mode were 0.5 secs for the LED on time and 2.5 secs for the off time, which is a 1:5 ratio. Alteration of the pulsing settings to 0.1 sec on and 1 sec off resulted in a 1:10 ratio, which resulted in improved signal-to-noise, and in observations which showed that these settings had the biggest effect in controlling the level of chloride oxidation. This equated to setting the terminal baseline parameter to 10 uA, above which value the sensitivity did not further improve and, additionally, chloride oxidation began to be observed. Further studies showed that increased off time did not significantly improve the sensitivity and consequently it was decided to maintain the 0.1 on and 1.0 off time in order to also achieve increased sample throughput.

Example 1

The determination of COD in seawater is presented. Results obtained by the pulsing method are compared to results obtained without pulsing.

Three examples are presented – COD analysis with direct light and no chloride present, COD with direct light and chloride present, and COD with pulsed light and

chloride present.

Figure 5a shows the normal response obtained for COD determination of 10 mg/L KHP with direct light with and without chloride present (at 1000 mg/L).

It will be seen that the tailing of the organic response down to its baseline is interrupted by the onset of the chloride oxidation. Since the response never returns to its baseline, the generation of an analytical signal is compromised.

Figure 5b shows the response for the solution analysed in 5a above, with the pulsed regime (chloride present).

For the pulsing regime, the protocol was as follows: with the current settings at 0.1 on and 1.0 off time, linearity was tested for a range of dilutions with seawater samples (See Figure 6). A 1:50 dilution of seawater without organic addition is seen to be preferred. Smaller dilutions are possible (i.e. 1:10), but they then require organic addition. With such high chloride backgrounds, and no organic present, chloride oxidation begins to dominate.

The results also showed that both the accumulated charges and resultant gradients of the calibration curves differed (see Figure 7a). When comparing saline and non-saline samples in pulsed mode, where the gradients are similar, but the accumulated charge is significantly different (figure 7b). The variation is due to variation in the ionic strength of in different electrolytes.

Example 2

Samples from a sugar refinery were analysed. Solutions were diluted 1:50 with electrolyte solution and subsequently analysed using a PeCOD™ L100 laboratory instrument, where the system was calibrated on 100 mg COD/L as sucrose.

The results are shown in Figure 8. These results determined by the PeCOD™ analyser closely resemble ($r = 0.995$) the trend exhibited by the BOD results.

Results for COD by the PeCOD™ technique show a linear correlation with BOD_5 (Figure 9) with a correlation coefficient of 0.995. This equates to a correlation multiplier of 0.48 to relate the measured PeCOD™ COD to a measured BOD_5.

In conclusion, the results show that the PeCOD™ COD method offers an appropriate method for real-time analysis of COD in salt water matrices. It also provides an accurate correlation with BOD_5, with a very high correlation coefficient of 0.995.

Overall the pulsing technique has proven itself to be a suitable technique to minimise chloride effects and to also handle solutions of varying salinity. The method of this invention has the following advantages compared to the prior art.

1. Organic addition is not essential;
2. No toxic mercury waste disposal is required;
3. The precipitation of chloride salts is avoided due to the suppression of photocatalytic activation of the chloride oxidation cycle;
4. The TiO_2 sensor life is extended due to pulsing efficiency of oxidation and the absence of chloride interference.
5. COD measurement is possible in the presence of inorganic counter ions.
6. COD measurement is possible in sea water.

Those skilled in the art will realise that the present invention provides a robust analytical tool that permits accurate measurement of COD in a short time and without the effects of interference from competing species such as chloride.

It will be evident to those practiced in the art that this novel new method also has potential application for other interfering species, such as other soluble counter ions (including bromides, iodides, sulphates, phosphates, etc.,) and for class speciation in various organic contaminants (e.g., those that have different rates and mechanisms of oxidation, molecular size, etc.)

Those skilled in the art will also realise that this invention may be implemented in embodiments other than those described without departing from the core teachings of the invention.

CLAIMS

1. A method of determining the chemical oxygen demand in water samples containing chloride ions by a photoelectrochemical method in which the photo electrode is activated by light pulses and in which the pulse parameters and the light source intensity are set to favour the oxidation of organic species in the water sample.

2. A method, as claimed in claim 1, in which the pulse duration is from 0.01 to 5 seconds and the interval between pulses is at least 1 second.

3. Water quality assay apparatus for determining oxygen demand of a water sample which consists of:
   a) a flow through measuring cell,
   b) a photoactive working electrode and a counter electrode disposed in said cell,
   c) a UV light source, adapted to illuminate the photoactive working electrode,
   d) a control means for the pulsed illumination of the working electrode, applied potential and signal measurement,
   e) a current measuring means to measure the photocurrent at the working and counter electrodes,
   f) a data processing means to derive a measure of oxygen demand from the measurements made by the photocurrent measuring means.

4. A water quality assay apparatus, as claimed in claim 4, in which the data processing means measures oxygen demand using the algorithm:

$$COD\ (mg\ /\ L\ of\ O_2) = \frac{Q}{4FV} \times 32000$$

Where F is the Faraday constant, while V is the sample volume and Q is the charge and

Qnet = $\sum$(QPulseTotal - QBlank) (for all n pulses).

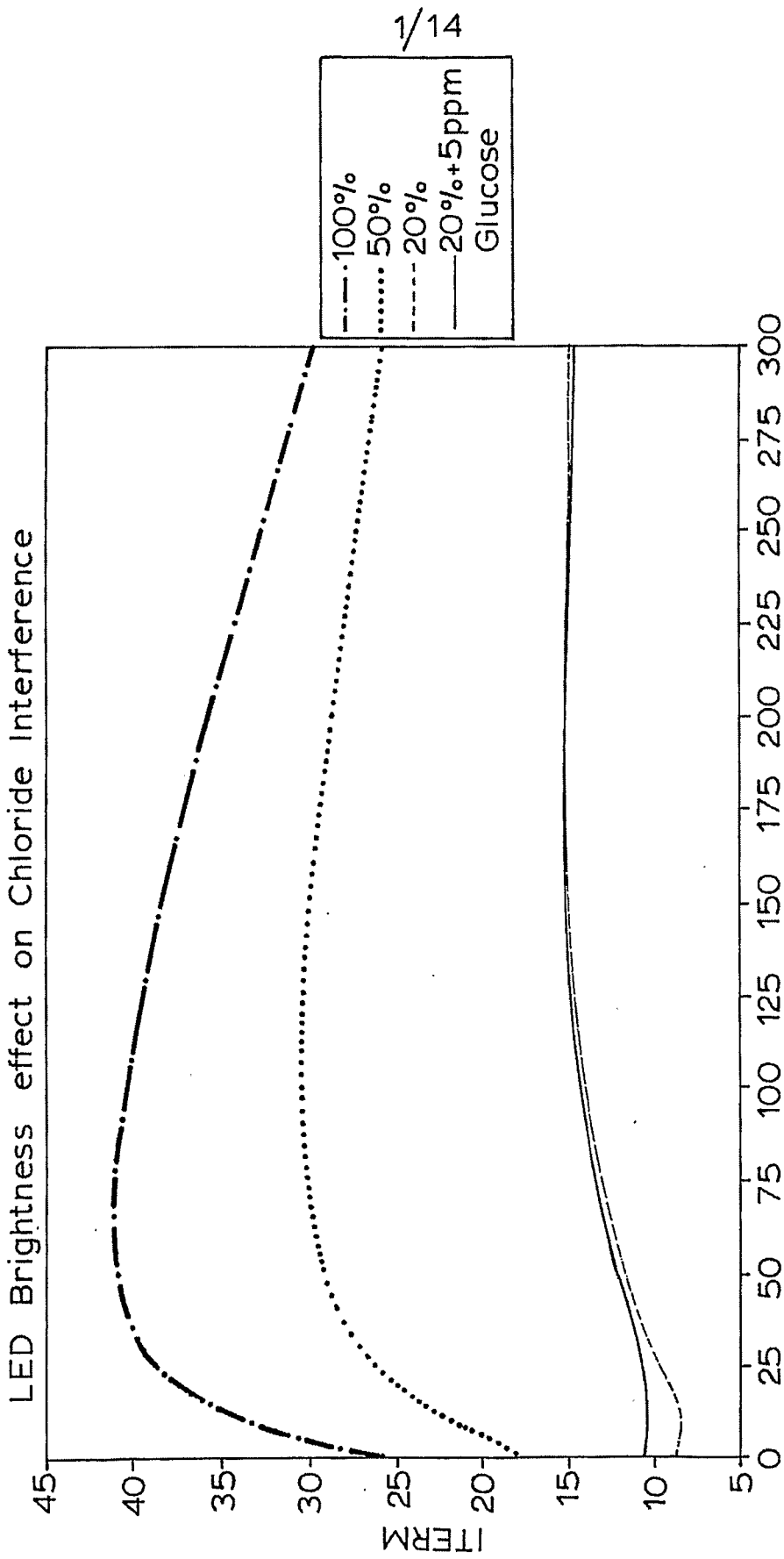
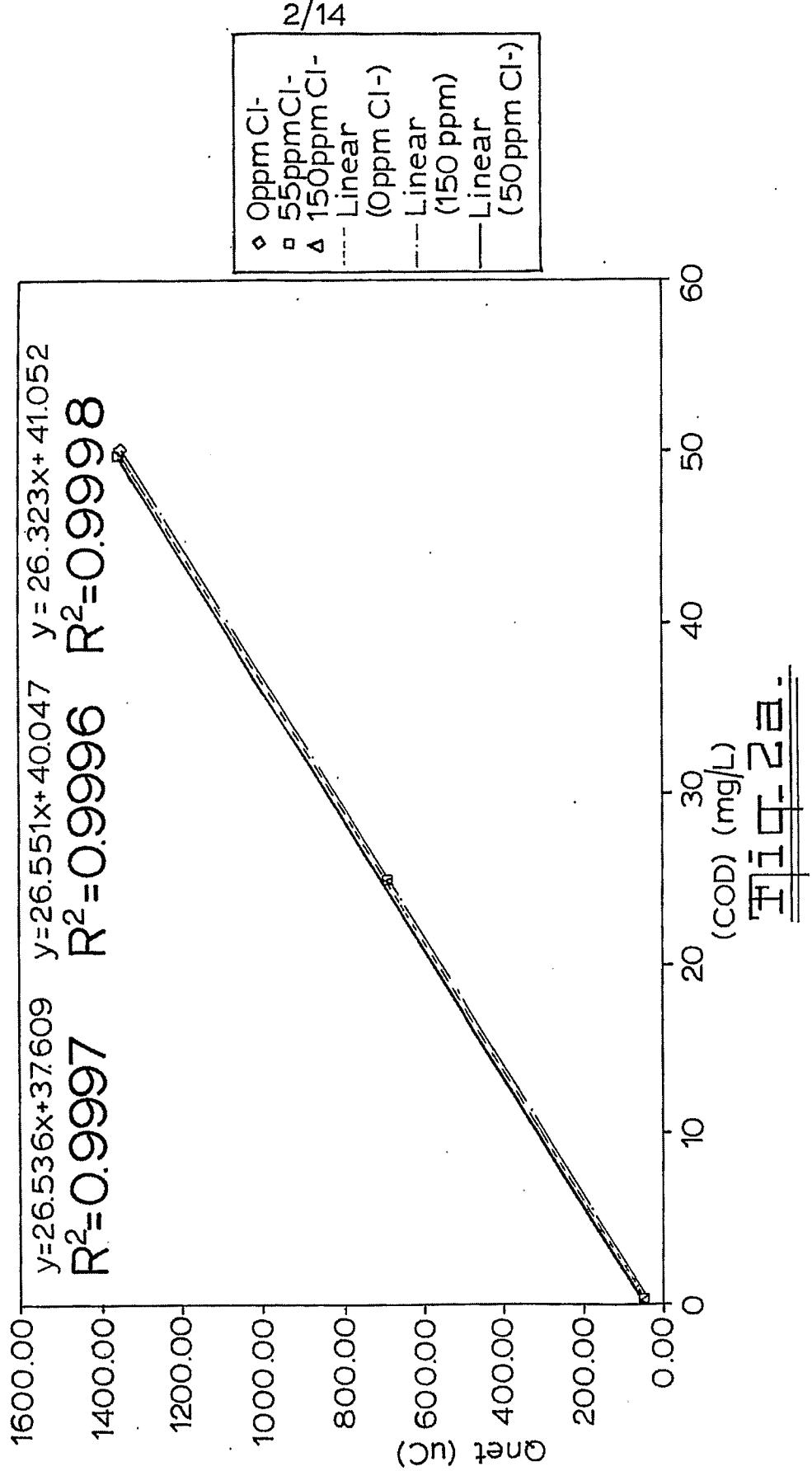


Fig 1 (PRIOR ART)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(COD) (mg/L)
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40
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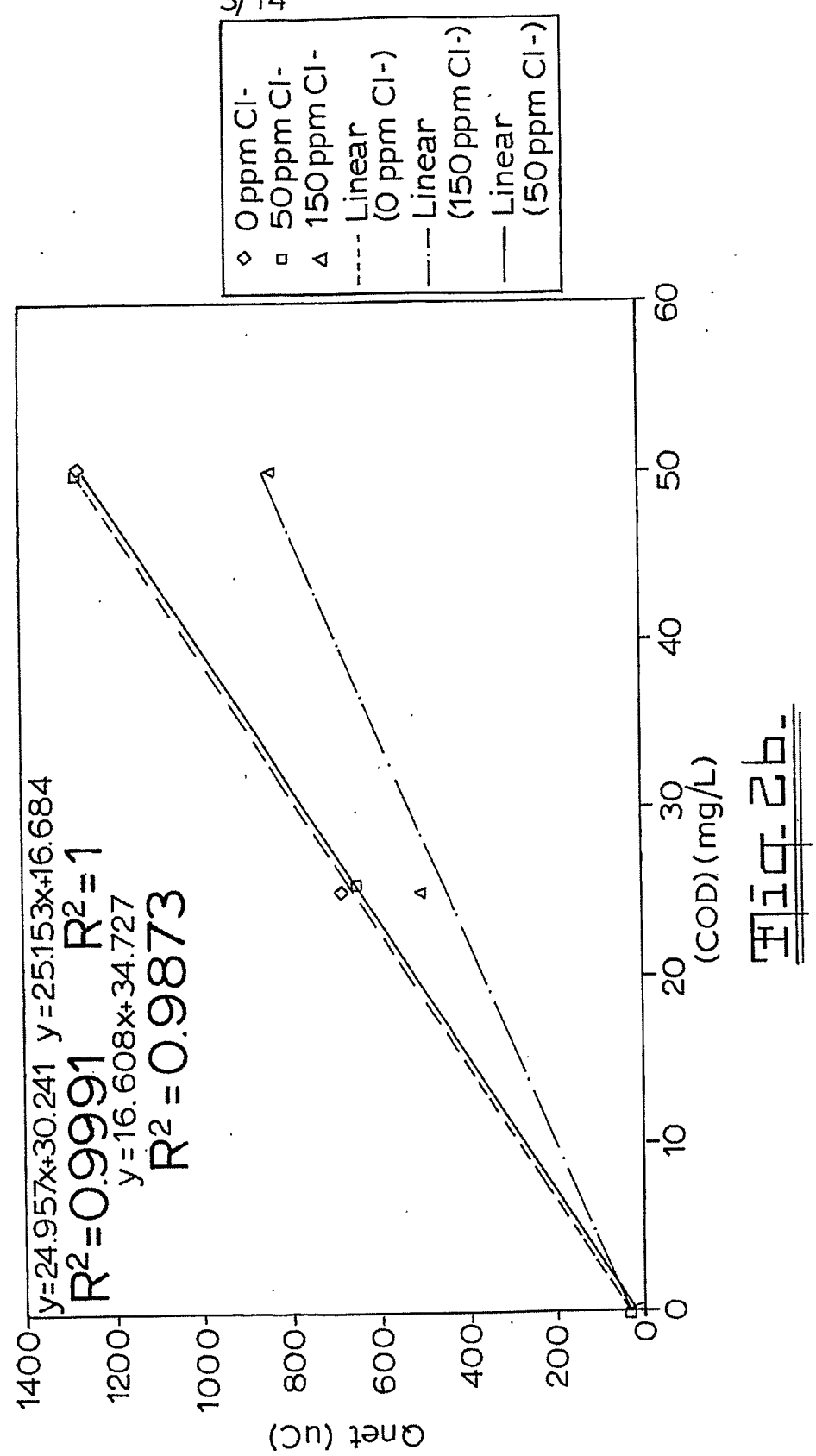
Fig 2a.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1200
1400
10
20
30
40
50
60

Fig. 2b.

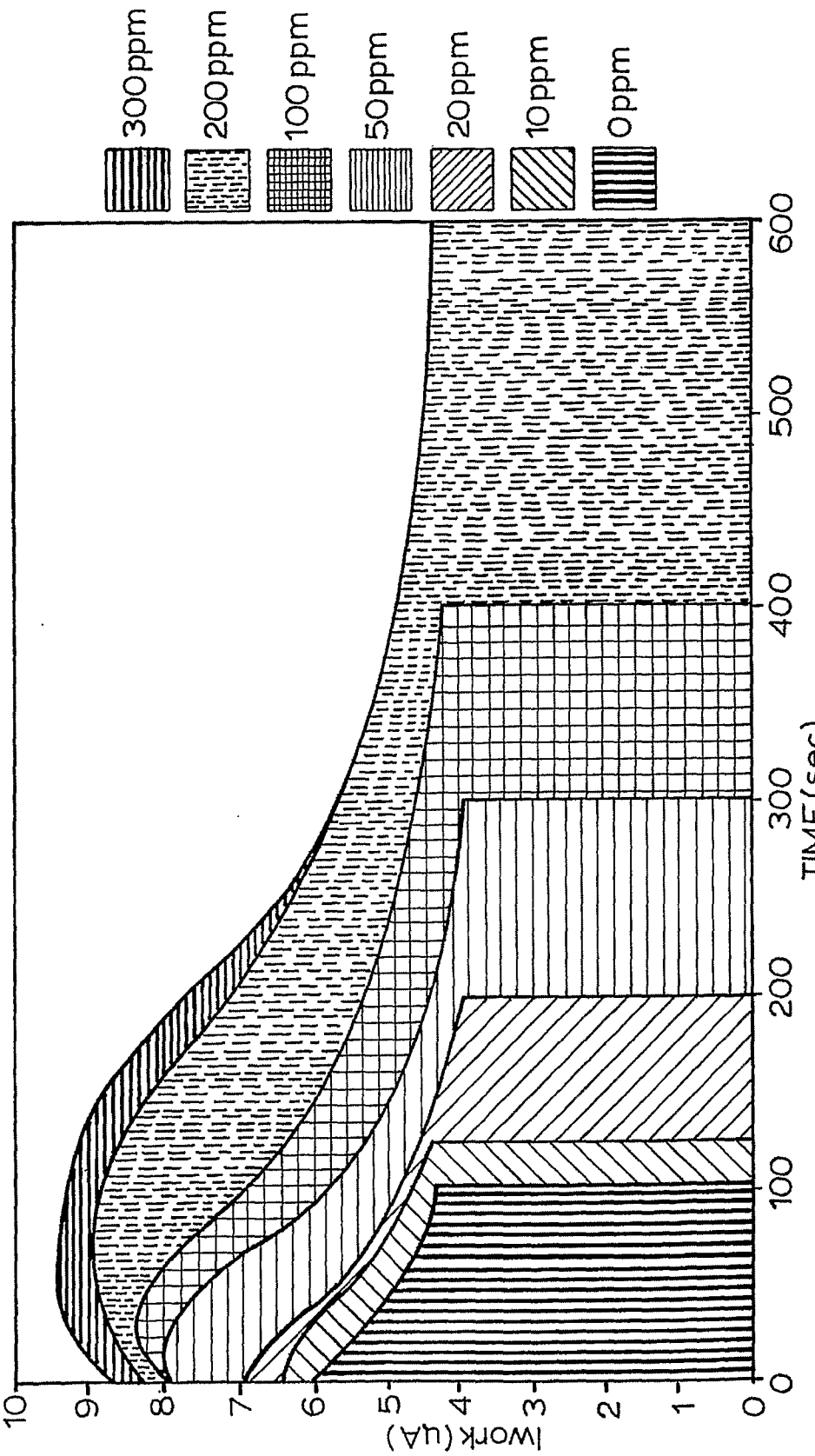
300ppm
200ppm
100ppm
50ppm
20ppm
10ppm
0ppm
Work (μA)
TIME (sec)
0
1
2
3
4
5
6
7
8
9
10
100
200
300
400
500
600

Fig. 3B.

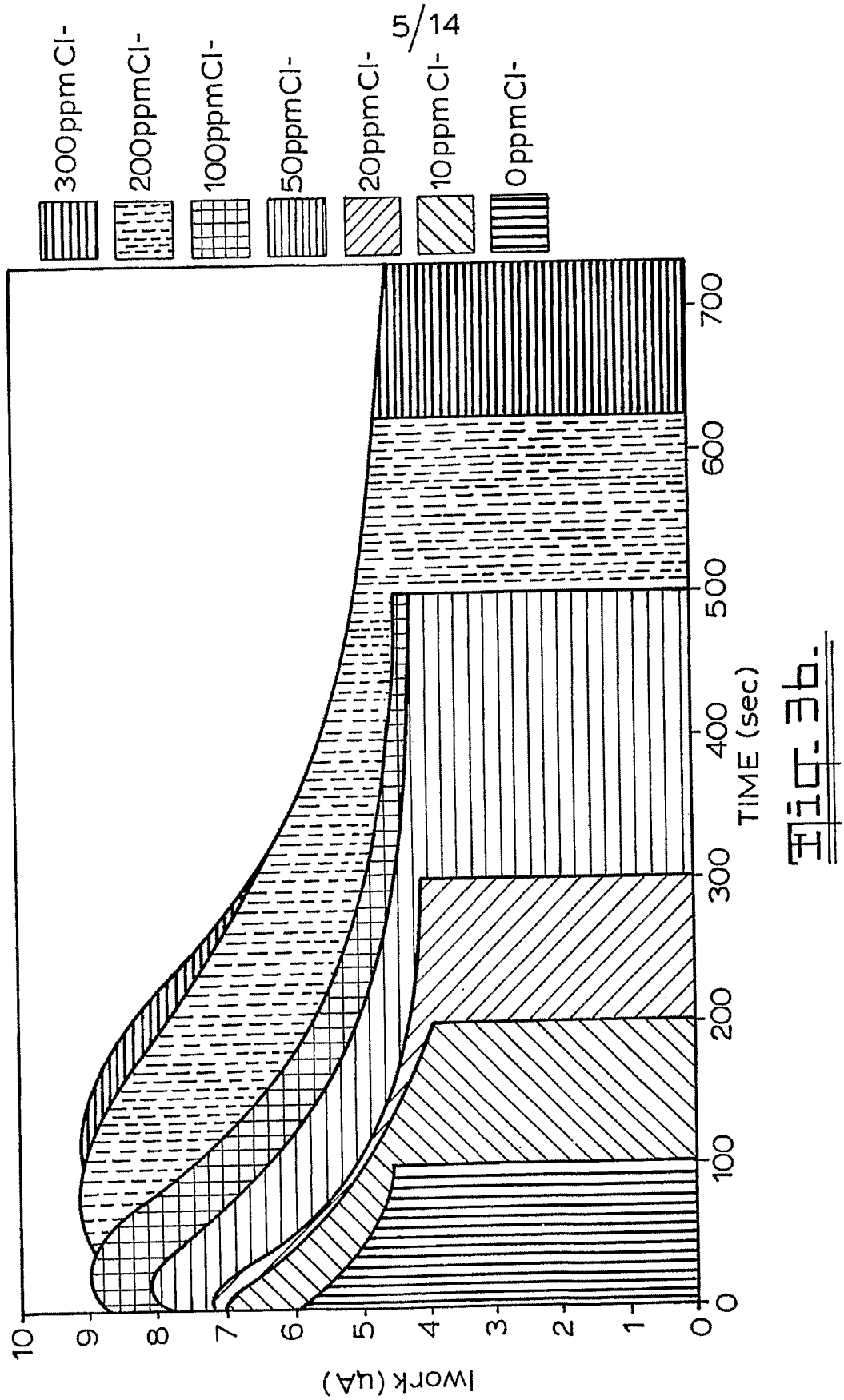
300ppm Cl-
200ppm Cl-
100ppm Cl-
50ppm Cl-
20ppm Cl-
10ppm Cl-
0ppm Cl-
Work (μA)
TIME (sec)
0
1
2
3
4
5
6
7
8
9
10
100
200
300
400
500
600
700

Fig. 3b.

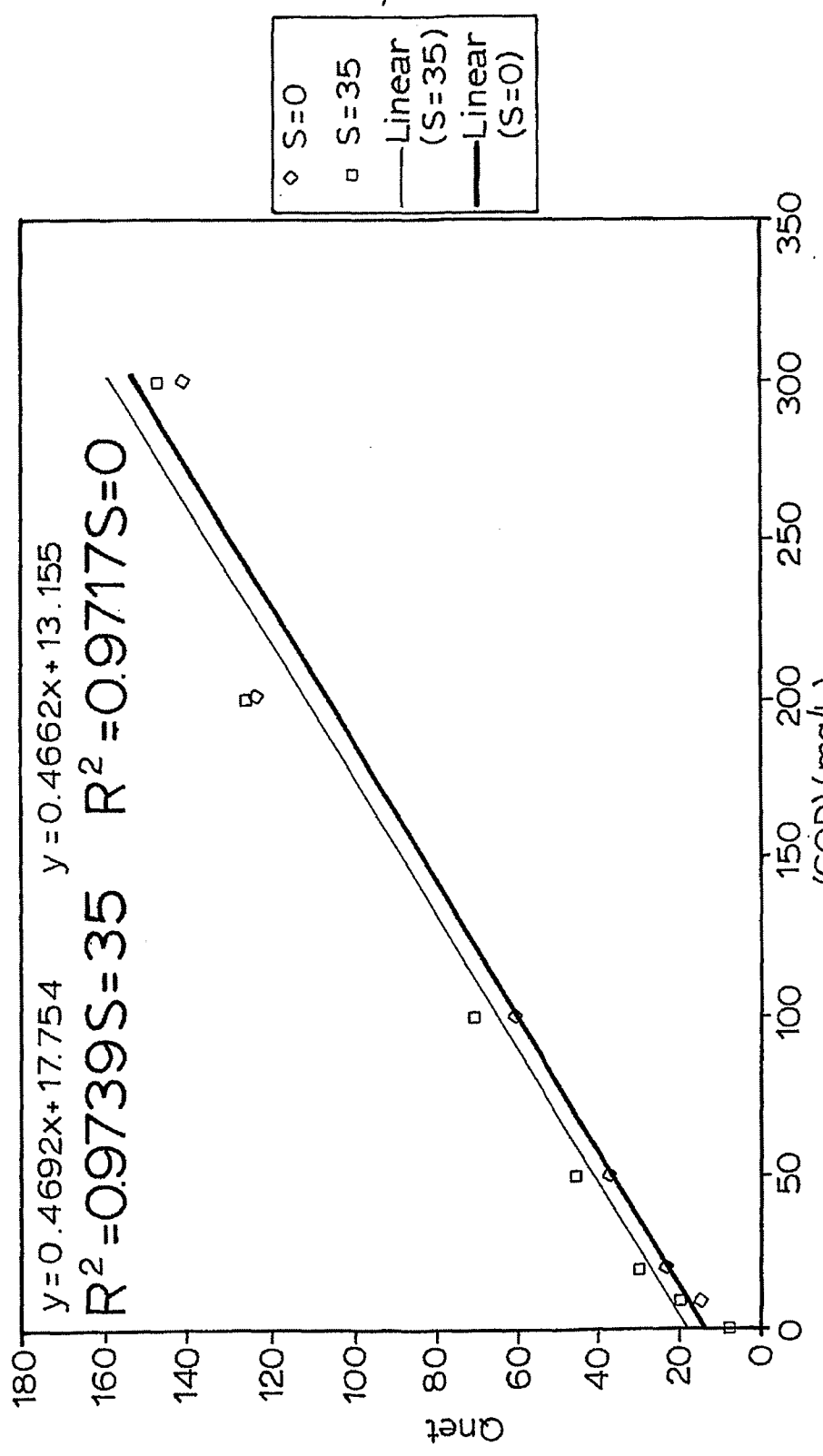
S=0
S=35
Linear (S=35)
Linear (S=0)
y = 0.4692x + 17.754
R² = 0.9739S=35
y = 0.4662x + 13.155
R² = 0.9717S=0
Qnet
(COD) (mg/L)
0
20
40
60
80
100
120
140
160
180
0
50
100
150
200
250
300
350

図4-4

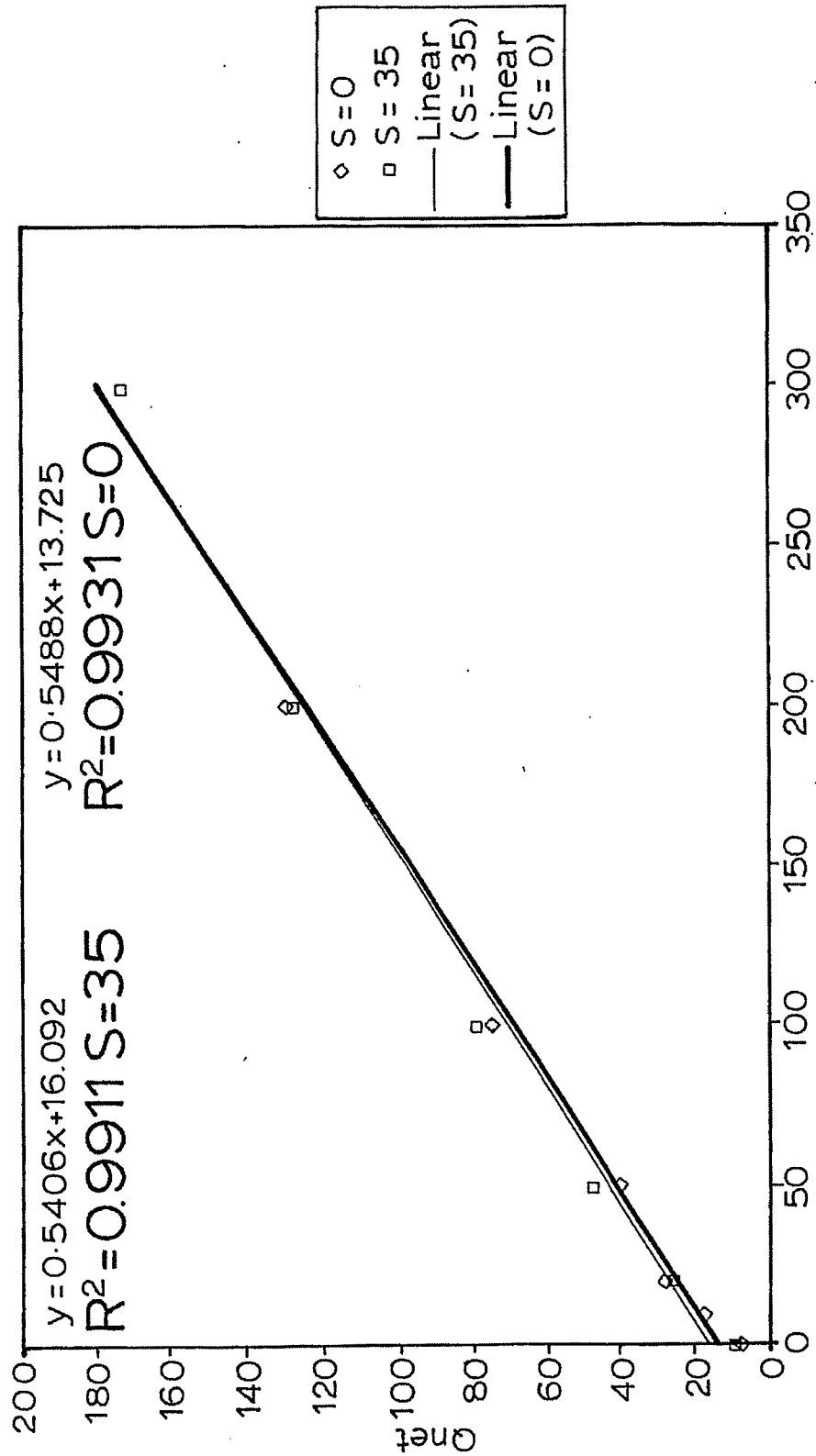
S=0
S=35
Linear (S=35)
Linear (S=0)
y=0.5406x+16.092
R²=0.9911 S=35
y=0.5488x+13.725
R²=0.9931 S=0
Qnet
(COD)(mg/L)
0
50
100
150
200
250
300
350
20
40
60
80
100
120
140
160
180
200

Fig 4b

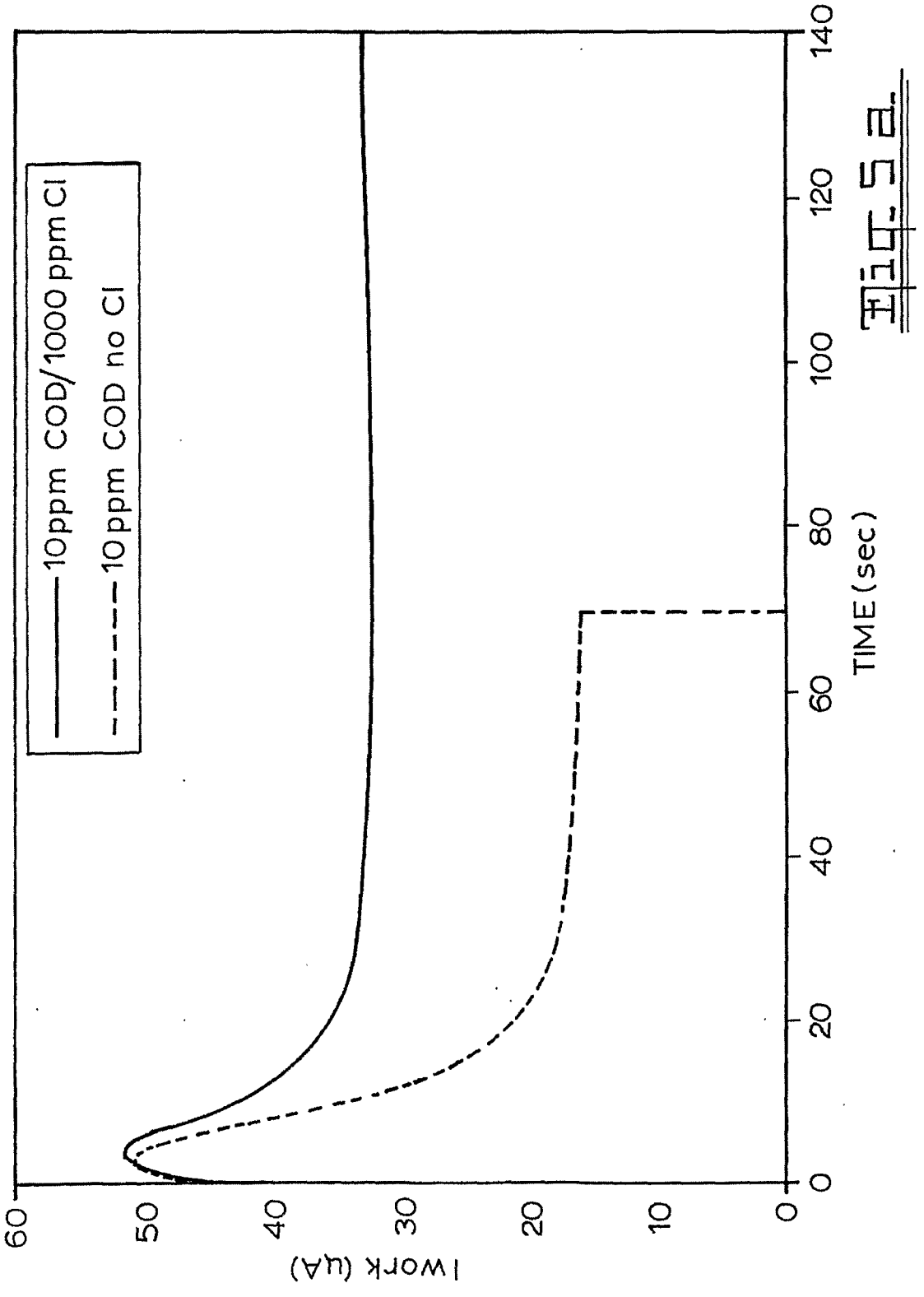
10ppm COD/1000 ppm Cl
10 ppm COD no Cl
Work (μA)
TIME (sec)
0
10
20
30
40
50
60
0
20
40
60
80
100
120
140

FIG 5a.

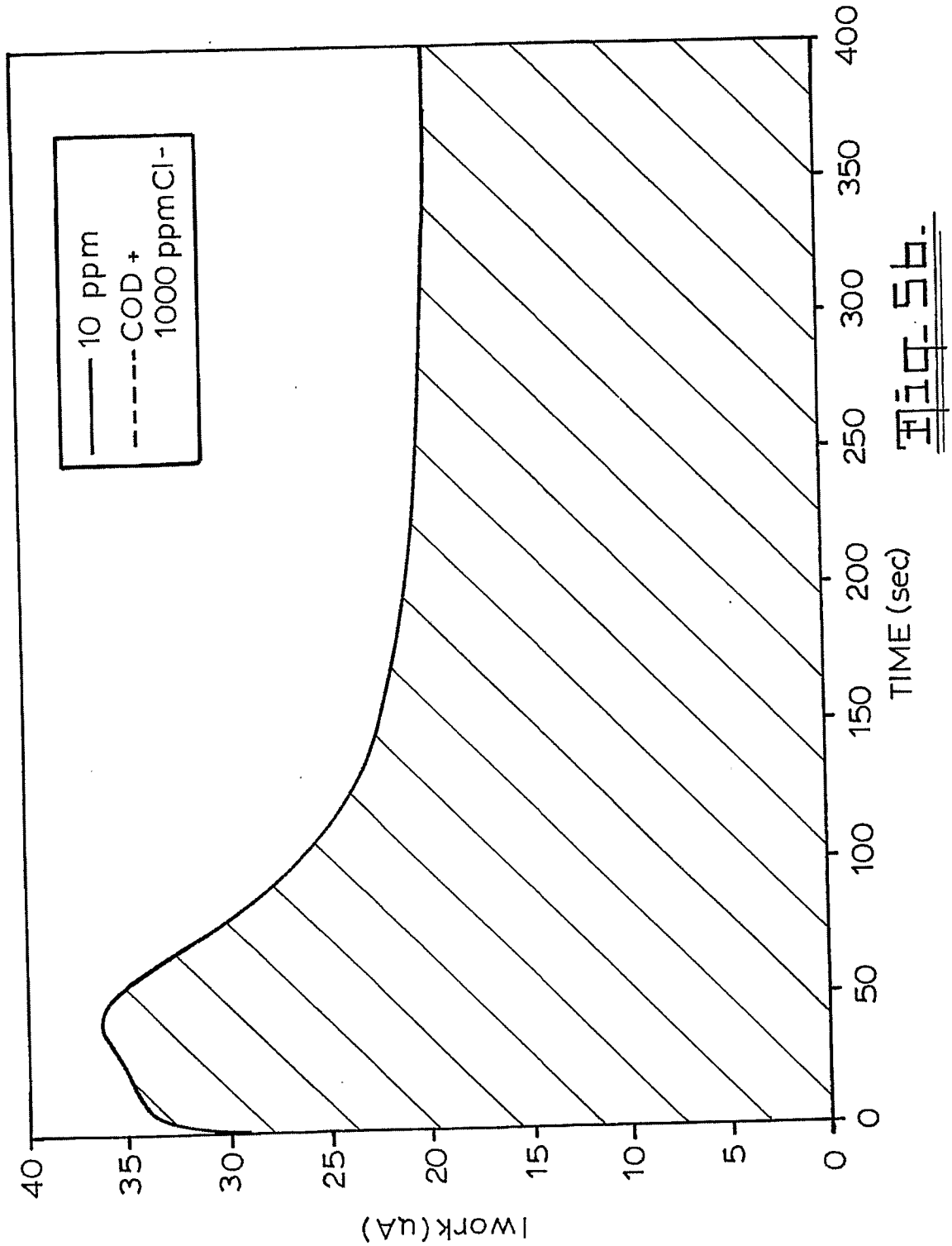
10 ppm
COD +
1000 ppm Cl-
Work (μA)
TIME (sec)
0
5
10
15
20
25
30
35
40
0
50
100
150
200
250
300
350
400

Fig. 5b.

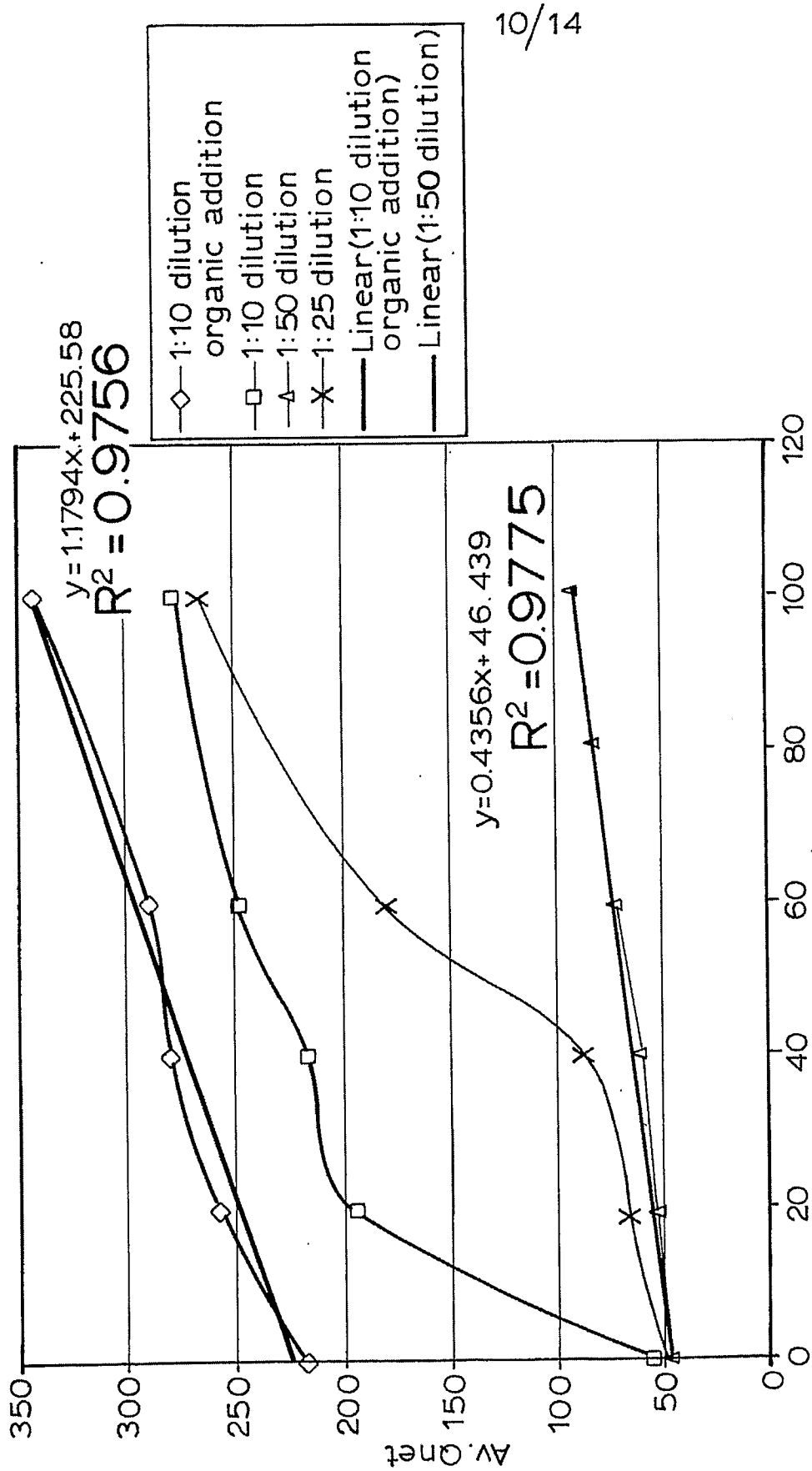
1:10 dilution organic addition
1:10 dilution
1:50 dilution
1:25 dilution
Linear(1:10 dilution organic addition)
Linear(1:50 dilution)
y=1.1794x+225.58
R2 = 0.9756
y=0.4356x+46.439
R2 =0.9775
Av. Qnet
(COD)(mg/L)
0
20
40
60
80
100
120
50
100
150
200
250
300
350

Fig 6.

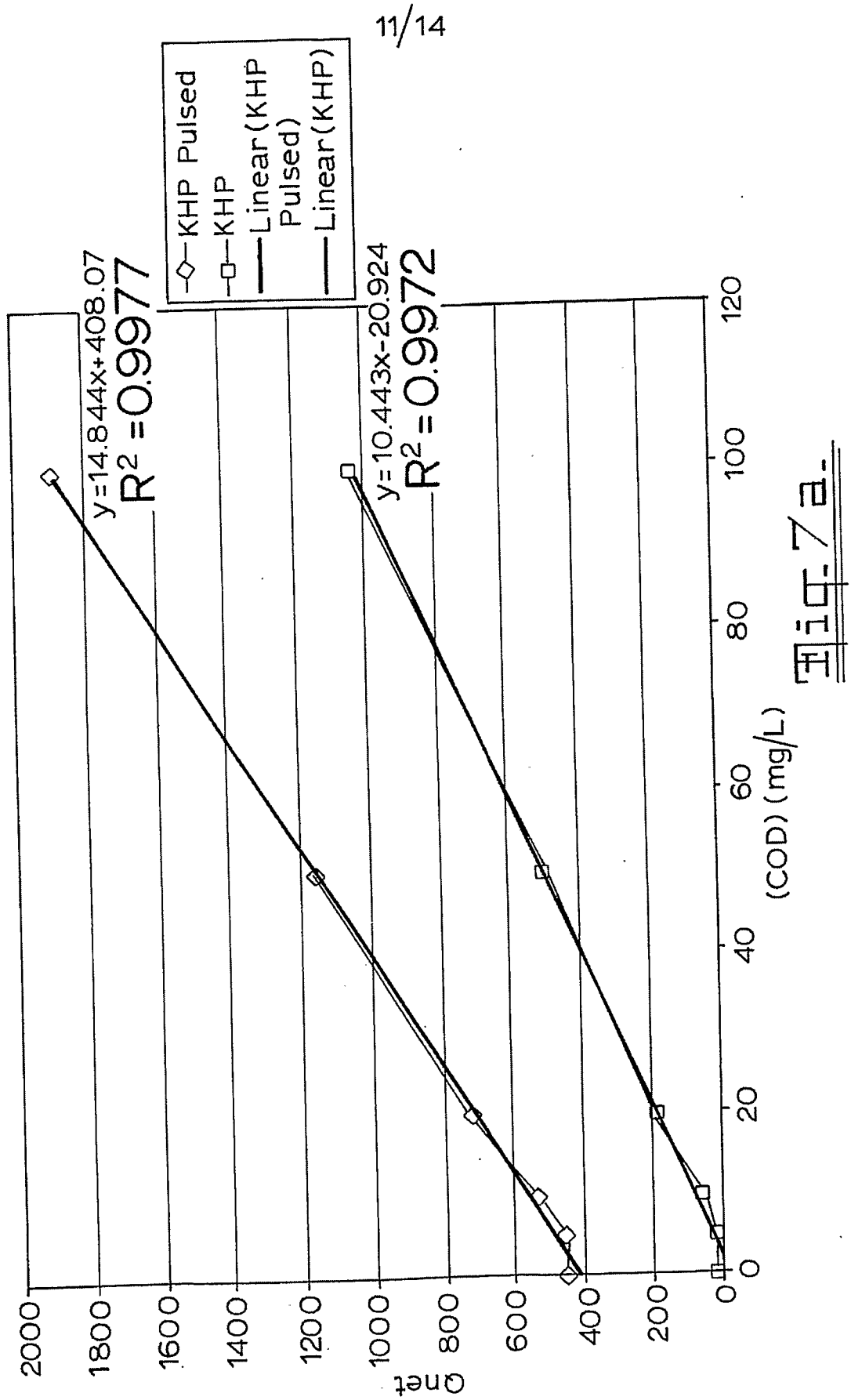
KHP Pulsed
KHP
Linear(KHP Pulsed)
Linear(KHP)
y=14.844x+408.07
R2 =0.9977
y=10.443x-20.924
R2 =0.9972
Qnet
(COD) (mg/L)
0
200
400
600
800
1000
1200
1400
1600
1800
2000
0
20
40
60
80
100
120

Fig. 7a.

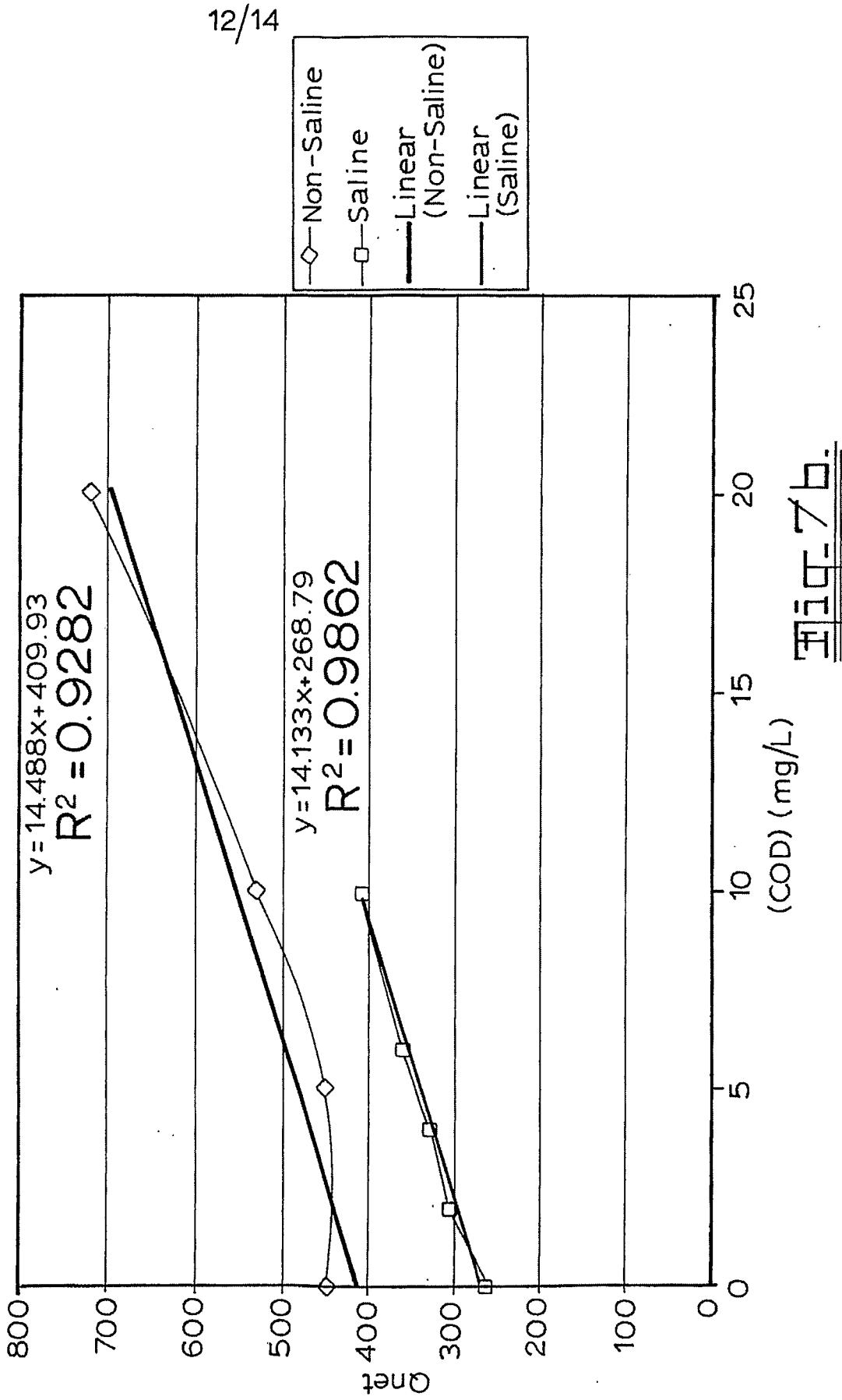
Non-Saline
Saline
Linear (Non-Saline)
Linear (Saline)
y=14.488x+409.93
R2=0.9282
y=14.133x+268.79
R2=0.9862
Qnet
(COD) (mg/L)
0
100
200
300
400
500
600
700
800
0
5
10
15
20
25

Fig. 7b.

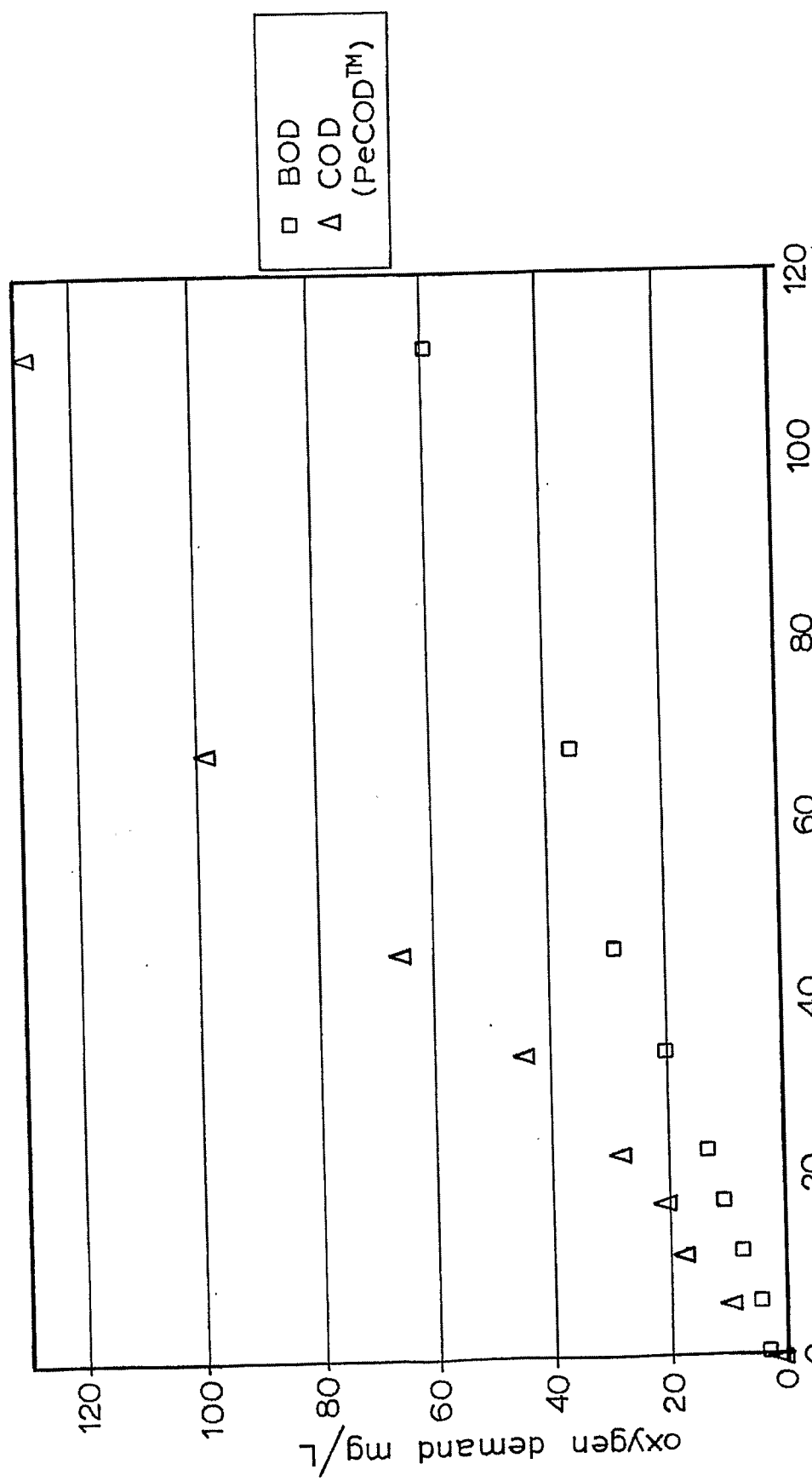
BOD
COD (PeCOD™)
oxygen demand mg/L
0
20
40
60
80
100
120
SAMPLE
0
20
40
60
80
100
120

Fig. 8

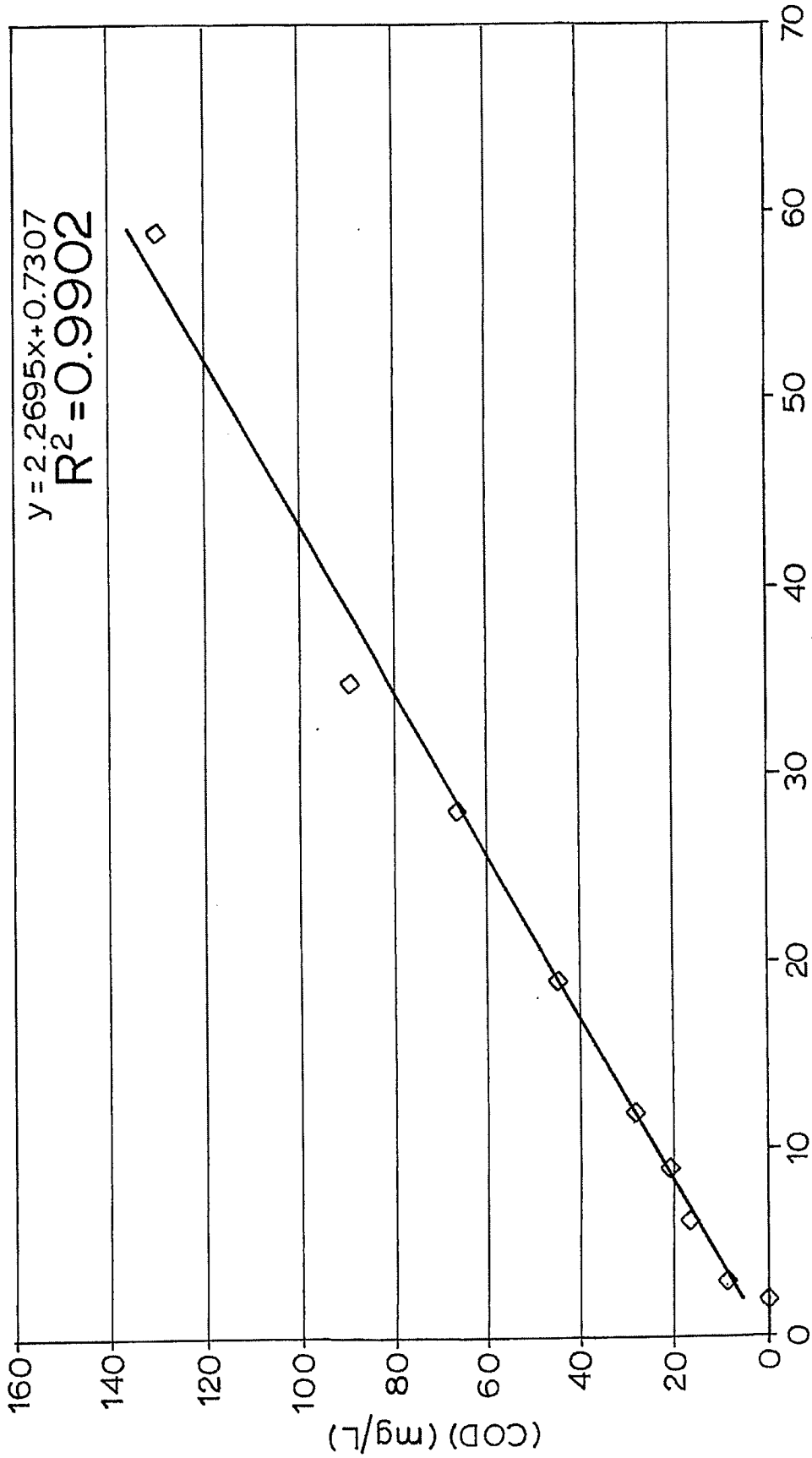
y = 2.2695x+0.7307
R² = 0.9902
(COD) (mg/L)
(BOD) (mg/L)
0
20
40
60
80
100
120
140
160
0
10
20
30
40
50
60
70

図1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2008/001529

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

G01N 27/30 (2006.01) ***G01N 33/18*** (2006.01)

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)

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 practicable, search terms used)
EPODOC, WPI: IPC: G01N plus keywords: oxygen, deplete, demand, degrade, reduction, exhaust, COD, PECOD, light, UV, ultra-violet, illuminate, beam, ray, radiation, pulse, intermittent, frequency, period, water, aqueous, H2O, photoelectrode.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2004/088305 A1 (GRIFFITH UNIVERSITY) 14 October 2004 Figure 8 and description	
A	WO 2007/016740 A1 (AQUA DIAGNOSTICS PTY. LTD.) 15 February 2007 abstract	

☐ Further documents are listed in the continuation of Box C ☒ See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04 December 2008	10 DEC 2008

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2008/001529

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
WO	2004088305	AU	2004225910	AU	2005220276	CA	2521395
		CN	1774627	EP	1611440	KR	20050120698
		NZ	542454	US	2006205083	US	2006240558
WO	2007016740	AU	2006279258	CN	101238364	EP	1913370
		KR	20080042076				

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX