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A Dip in the Dribble

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A Dip in the Dribble

20th May

All flora and fauna in the River Dribble
south of the town of Sheepsdale
has been suddenly killed off.

**Use the information given on the
clue cards to determine the
cause and nature of the incident.**

A Dip in the Dribble

SCIENTIFIC SKILLS

- environmental issues
- industrial chemistry
- pollution
- organic analytical techniques
- handling information
- toxicity
- costing services

TRANSFERABLE SKILLS

- working with others
- communication
- decision making
- analytical/critical thinking
- independent learning
- time management
- budgeting and economics

What you need to do

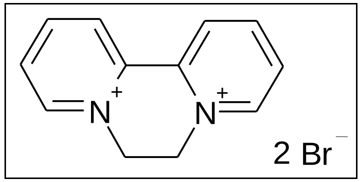
Part 1 - Consider:

- Whether there is a problem
- Where and when it occurred
- The nature and source(s) of the pollution
- The toxicity of the pollutants
- Who could be at fault

Part 2:

- Commission a monitoring programme

The chemical structure of Diquat dibromide is:



Water Solubility	70% w/v @ 20 °C
Vapour Pressure	Negligible @ 20 °C
Partition Coefficient	4.6021
Absorption Coefficient	13000 $dm^3\ mol^{-1}\ cm^{-1}$ at 310 nm

In water paraquat dichloride and diquat dibromide are completely dissociated into PQ^{2+} + 2 Cl^- and DQ^{2+} + 2 Br^-.

Analysis of an isolate from River Dribble from Environment Agency sample point on 20th May showed a compound of molecular weight 184.

The Environment Agency sample point is 2 km west of Sheepsdale

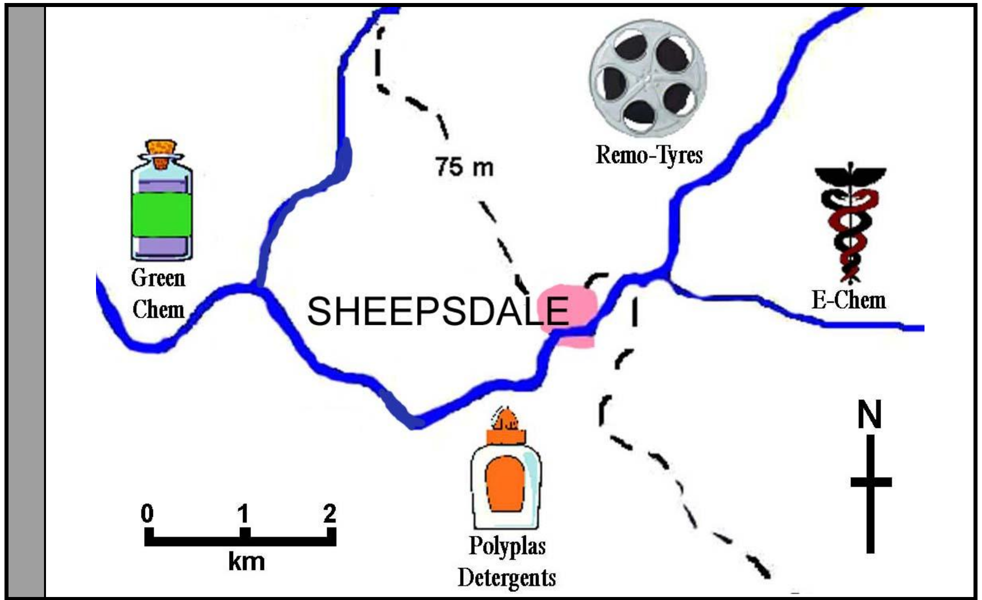
Introducing Dr. Orlando Grut of

E-Chem Ltd.

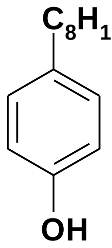
Specialists in Agrochemicals and Chemical Surfactants.
Agents for Aquascrap, Aquaslay, Dextrone, Veglone,
Smeglox, Merit, Cruise, Trident, and BLX Agrocultural.

Telephone 0100 000 666

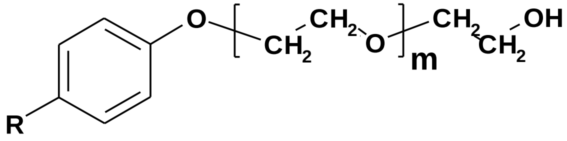
Midwives working in the Sheepsdale area noticed an unusually high number of miscarriages in the previous August.



Dairy farmer Nobby Giles owns a field that is bounded by the river Dribble. On 20th May four of his young calves that were grazing in the field were found dead.



4-octylphenol

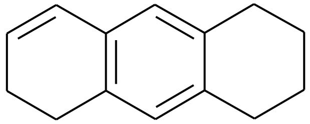


alkylphenol polyethoxylate

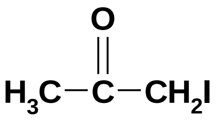
Alkylphenol polyethoxylates are widely used as industrial, household and surfactants.

The Dairy Farmer

"Dr. Sidney Spittle has reported that increased miscarriage rates may be linked to pesticide residues in milk and related products."



1,2,3,4,5,6
hexahydroanthracene



$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2I$

iodoacetone

A surfactant is a species that is active at the interface between two phases such as the interface between hydrophilic and hydrophobic phases. A surfactant accumulates at the interface and modifies the surface tension.

Analysis of an isolate from the River Dribble from the Environment Agency sample point on 20th May showed a compound that had an aromatic moiety.

Atomic weights of selected elements

C	12.01
H	1.008
Mg	24.30
Ca	40.08
N	14.01
O	16.00
Cl	35.45
Br	79.90
I	126.9

Polyplas Detergents make common industrial surfactants.

You are Marge Fugal-Horn

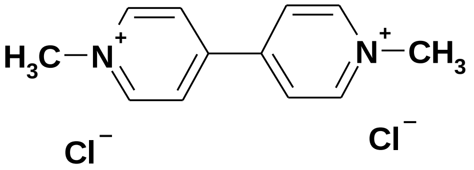
You live close to the E-Chem Ltd. packaging and warehouse facility. You wish you had not hung out your favourite dress to dry on 19th May.

You are Rick Niblett (date of birth 18/5/60). You wish you hadn't got quite so drunk on your birthday because you are hung over and fuzzy headed and so forgot to switch off the heated shrink wrapping machine that you operate before you went to tea break.

Diquat dibromide is moderately toxic via ingestion, with reported oral LD_{50} values of 231 mg/kg in rats, 125 mg/kg in mice, 101 mg/kg in rabbits, and 100 mg/kg in guinea pigs and dogs. Cows appear to be particularly sensitive to this herbicide, with an oral LD_{50} of 30 to 56 mg/kg.

Paraquat has been found to have a high affinity to suspended or precipitated sediment in the aquatic environment. Paraquat is significantly more toxic than its closely related compound diquat. A typical half-life for desorption of this chemical is 52 weeks.

Paraquat dichloride



Water Solubility	>50% w/v @ 20 C
Absorption Coefficient	18000 $dm^3\ mol^{-1}\ cm^{-1}$ at 257 nm
Vapour Pressure	Negligible @ room temperature as paraquat dichloride
Partition Coefficient	4.4683

April

Farmers Weekly:

"Disturbances were caused at the local Sheepsdale NUF meeting by protestors demonstrating against the increasing volumes of herbicides in use locally to combat the unusually high occurrence of chick weed found this year in fields containing oilseed rape."

17th May

Police report

"Intruders reported at E-Chem Ltd. packing and warehouse facility in the early hours of Friday morning. On arrival, no intruders were present and the warehouse manager believed no theft to have taken place. There was however a considerable degree of criminal damage."

Jan 13th

Sheepsdale Times

“The long awaited opening of the ‘Green Chem Agrochemical’ manufacturing plant finally took place last Thursday, officiated by Sheepsdale town Mayor Norman Fitzwilliam-Splat. Referring to the long wrangling over health and safety issues which had delayed the opening of the plant, Mr Fitzwilliam-Splat remarked that whilst he understood that the road to the realisation of the project had been bumpy, he now hoped that the plant “could get to work and provide much needed employment to the Sheepsdale locality. The plant will be principally involved with the manufacture of agrochemicals such as paraquat.”

You are Dr Algernon Bloom

You have been called in by the Environment Agency to investigate the death of vegetation in the River Dribble. Upon investigation you find that there are higher than expected nutrient levels in the river north of Sheepsdale.

You are Dr Edwin S Cargo

You have been called in by the Environment Agency to investigate the death of vegetation and fish in the River Dribble.

Upon investigation, you find no unusual organisms in the river which may have resulted in the death of the flora and fauna. However, there is a slight increase in the number of snails North of Sheepsdale.

You are Terry Grimsdale

On May 19th your wife, Audrey, was rushed into hospital after going into labour prematurely.

Snails graze on the algae found in freshwater vegetation.

You are are Samantha Ridcully

You and your friend Audrey Grimsdale have been protesting without success about Nobby Giles' Dairy Farm. You both run a vegan restaurant in Sheepsdale.

Veglone

Targets: Pre-harvest crop desiccant, certain broad-leaved weeds, and certain water weeds.

Indications:

Crops (Desiccant)	Maximum individual dose
Potatoes	10 l/ha
Oilseed rape	4 l/ha
Barley & oats for feed stock	3 l/ha
Peas for harvesting dry	4 l/ha
Field beans	4 l/ha
Clover for seed	5 l/ha
Linseed	9 l/ha

Important: Ingredients as follows: Liquid formulation containing 200 g/l (16% w/w) diquat as dibromide salt.

999 call list obtained from co-ordination centre at Sheepsdale 19th May

Incident	Time	Service Required
Suspected heart failure	7.00 am	Ambulance
Lorry accident. Articulated lorry jack-knifed at Thrifty bridge. Driver trapped in cab. Possible spinal injury. Lorry believed to be carrying hazardous materials.	7.45 am	Ambulance Fire Police
Drugs overdose	8.30 am	Ambulance
Fire at warehouse	10.00 am	Ambulance Fire Police
Baby delivery	10.30 pm	Ambulance
Baby delivery	11.15 pm	Ambulance

999 call list obtained from co-ordination centre at Sheepsdale 12th May

Incident	Time	Service Required
Prolapsed bladder	7.15 am	Ambulance
House fire – possible inhalation of toxic fumes	7.45 am	Ambulance Fire
Patient complaining of severe stomach pains together with skin rash and intermittent loss of consciousness	8.00 am	Ambulance
RTA – 3 car pile up	8.30 am	Ambulance Fire Police
Cat up tree	10.30 am	Ambulance Fire Police
Child with head stuck in toilet cistern	10.45 pm	Ambulance

Scramoxene

Targets: Grass weeds, broad-leaved weeds

Uses	Maximum individual dose
Around farm and non-cropped areas	5.5 l/ha
Autumn sown crops – pre-drilling or pre-emergence	4 l/ha
Grassland – pre-ploughing, direct drilling of reseeding	8.5 l/ha
Horticultural crops	5.5 l/ha
Potatoes – early emergence	5.5 l/ha
Spring sown crops	5.5 l/ha
Stubble clearing	3 l/ha

Toxicology	Skin contact: irritating to skin. It is not a skin sensitiser Eye contact: Irritating to eyes Ingestion: PARAQUAT CAN KILL IF SWALLOWED
Active ingredients:	liquid formulation containing 160 g/l (14.4% w/w) paraquat as dichloride salt.

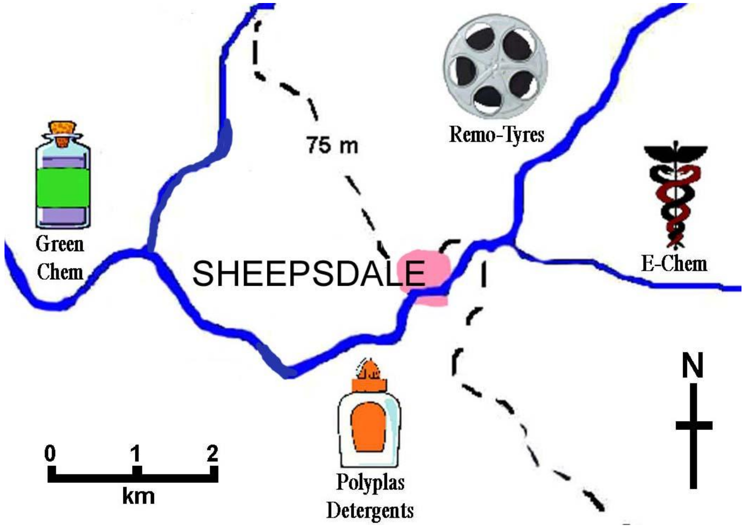
Extract from circular letter sent to all companies requesting discharge consents into the River Dribble and tributaries:

“With reference to the ongoing review of discharge consents. The agency has decided, in consultation with the Department of the Environment, that no discharge consents will be issued in respect of discharges into the River Dribble. It has also been decided that a review of current drainage networks be undertaken.”

Implications of a Warehouse Fire

E Chem Ltd own a chemical works, warehouse and dispatch centre just east of Sheepsdale. On 19 May, an incident occurred where a shrink-wrap machine that operates at high temperatures was left on during a coffee break and started a fire in the warehouse. The majority of the chemicals stored in the warehouse at the time of the fire were herbicides, of which the main component was diquat dibromide. The chemical *p*-octylphenol as dry flake in 40 x 25 kg paper sacks on pallets was being shrink-rapped. It is used in the manufacture of surfactants.

Map of the Sheepsdale area



The fire was discovered at 10 am in part of the warehouse and the fire brigade was called. By the time they had arrived at 10:15 a.m. the fire had spread. The fire crews immediately tackled the fire, using a nearby water hydrant as a source of water. The fire spread rapidly into other areas. The fire was finally brought under control and doused at 1 p.m. The warehouse contained *p*-octylphenol stored on pallets and 75 x 200 litre drums of diquat dibromide.

Drains on the premises discharge into a local beck (a small stream) and subsequently into the River Dribble. It can be assumed that the water used to douse the fire exited the premises *via* this route.

20th May

Sheepsdale Times & Courier

Town rocked: Chemical Catastophe

Hormones escape into the Dribble causing fear of lasting damage to the townsfolk of Sheepsdale

At about 10 am on Saturday morning the fire service was called to a fire at the E-Chem chemical storage warehouse to the north of Sheepsdale. The fire occurred in the storage section of the works where chemicals used to manufacture and prepare herbicides for use all over the world are stored.

The Sheepsdale part time fire service gallantly battled the fire for over three hours before the blaze was finally brought under control. At this point it was discovered that the massive use of water to douse the intense blaze had washed chemicals into a nearby beck

This morning environmental experts are on site assessing any long term damage. According to Dr. Miller of Midshire University, “The presence of an alkyl-phenol has caused grave concern because this chemical simulates the affects of oestrogens.”

Paul Smythe, a local fisherman said, “Some female fish caught on the weekend had male genitalia!”

One man claims that a bull seen drinking water from the beck grew udders in a few minutes.

A spokesman from the works refuted these claims but would not comment on the long term affects of the chemical. Meanwhile, whilst the effects of the hormone like substance are not known, there is also concern that large quantities of the herbicide diquat dibromide, which is closely related to paraquat, has also been washed into the beck. The possible consequences of the release are all too clear.

Eric Sydenham Cowry, prize marrow grower, and local councillor, said today "Bye tis a bad day and no mistake. I've ' ad bes' marro's round 'ere for thirty years and to look at ' em this morning you' d think there' d been a nuclear war.

Write a report to brief the chief investigator. This should include the following background information (no more than 2 sides of A4):-

1. The name, structure and main uses of the chemicals involved in the fire?
2. A discussion of the hazards associated with the chemicals and the precautions to be used when using these compounds.
3. A discussion of the effect of diquat on plant life. Explain the chemistry.
4. An explanation as to why the release of *p*-octylphenol into the environment gives cause for concern?

Environmental Analysis (1)

Diquat dibromide and *p*-octylphenol have the potential to cause short-term and long-term damage to the environment. Therefore, it is important to consider the measurement of the concentrations of the chemicals immediately after the incident and their subsequent fate. The majority of the chemicals were discharged into the environment via the drains on the site and then into the beck.

Discuss in your groups:
- The type, frequency and number samples that would be required.
- Those who could be prosecuted for the escape of pollutants into the River Dribble. Give your reasoning.
- Those who would be liable to pay for the monitoring of the pollution and subsequent clean up operations.

Assume that a monitoring programme is being set up for this river system. Your task is to produce recommendations for the implementation of the monitoring programme.
- Prepare a brief presentation outlining an analytical method found in the literature that could be used to detect diquat dibromide and *p*-octylphenol (one for each).
- Enclose a photocopy/print out of the first page of the most recent paper you have found for each chemical.

Notes

Environmental Analysis (2)

Diquat dibromide and *p*-octylphenol have the potential to cause short-term and long-term damage to the environment. Therefore, it is important to consider the measurement of the concentrations of the chemicals immediately after the incident and their subsequent fate. The majority of the chemicals were discharged into the environment via the drains on the site and then into the beck.

Discuss in your groups:

- The type, frequency and number samples that would be required.
- Those who could be prosecuted for the escape of pollutants into the River Dribble. Give your reasoning.
- Those who would be liable to pay for the monitoring of the pollution and subsequent clean up operations.

Assume that a monitoring programme is being set up for this river system. Your task is to produce recommendations for the implementation of the monitoring programme.

- Produce a short presentation reviewing analytical methods that could be used to detect diquat and *p*-octylphenol based on the abstracts provided.

Notes

1997

A.	**Diquat dibromide**
Journal	Galceran MT, Carneiro MC, Diez M, Puignou L (1997), 'Separation of quaternary ammonium herbicides by capillary electrophoresis with indirect UV detection,' Journal of Chromatography A, 782 (2): 289-295
Abstract	Suitability of various absorbent carrier electrolytes for the determination of quaternary ammonium ion herbicides ('quats') with indirect UV detection in capillary electrophoresis was investigated. Consideration of the electrophoretic mobility and the molar absorptivity of the chromophore, and the effective separation achieved, suggested that 1-(4-pyridyl)pyridinium chloride hydrochloride (PP) was the best electrolyte for the simultaneous detection of quats. The influence of pH, chromophore concentration, organic modifier, detection wavelength and ionic strength was investigated. The optimal conditions for separation were: 10 mM PP (pH 2.5), 10% methanol as carrier electrolyte, applied potential +20 kV, hydrodynamic injection 5 s and UV detection at 205 nm. Figures of merit such as detection limits and run-to-run and day-to-day reproducibility were established. The detection limits for the non-absorbent herbicides were 0.8 mu g ml(-1). The method was successfully applied to the determination of chlormequat and mepiquat in spiked tap water although the dependence of the detection limits on the sample matrix was observed.

B.	**Diquat dibromide**
Journal	Walker_PA, Shaver_JM, Morris_MD, (1997), 'Identification of cationic herbicides in deionized water, municipal tap water, and river water by capillary isotachophoresis / on-line raman spectroscopy,' *Applied Spectroscopy*, 51(9), 1394-1399
Abstract	Isotachophoresis (ITP), coupled with Raman spectroscopic detection, is used to separate and identify two cationic herbicides, paraquat and diquat, in spiked deionized water, municipal drinking water, and river water samples. On-line preconcentration is achieved with the use of field-amplified injection into a 0.03-0.1 M H_2SO_4 or Na_2SO_4 leading electrolyte solution, and isotachophoresis is achieved with the use of a 0.03-0.1 M tris(hydroxymethyl)-amino-methane (Tris) trailing electrolyte solution. The herbicides are concentrated to above 10^{-3} M at the detection window, allowing measurement of Raman spectra with 1-s integration windows. Spectra of the herbicides are obtained from solutions at initial concentrations in deionized water at 3.5 x 10^{-7} M (90 ppb) paraquat/5.8 x 10^{-8} M (20 ppb) diquat, from drinking water initially at 1.3 x 10^{-6} M (335 ppb) paraquat/1.0 x 10^{-6} M (360 ppb) diquat, and river water initially at 5.0 x 10^{-6} M (1.3 ppm) paraquat and 3.0 x 10^{-6} M (1.0 ppm) diquat. The utility of correlation to identify the presence of analytes and of factor analysis to recover spectra from solutions at low initial concentrations of the herbicides is demonstrated.

C.	**Diquat dibromide**
Journal	Marr_JC, King_JB, (1997), 'A simple high performance liquid chromatography ionspray tandem mass spectrometry method for the direct determination of paraquat and diquat in water,' *Rapid Communications in Mass Spectrometry*, 11(5), 479-483
Abstract	A method has been developed for the direct determination of paraquat and diquat in water samples. No sample preparation was required and analysis was done using high performance liquid chromatography coupled,vith ionspray tandem mass spectrometry, Heptafluorobutyric acid was used as the ion-pair agent. Further improvements in this method included the incorporation of an internal standard (caffeine). Using this method, detection limits of 5 and 1 mu g/L were obtained for paraquat and diquat respectively, Recoveries were consistently > 90% with relative standard deviations of < 10% over the concentration range 5-100 mu g/L. To our knowledge, this method is the first application of ionspray tandem mass spectrometry, and the first to use heptafluorobutyric acid as an ion-pair reagent, for the analysis of paraquat and diquat.

D.	**Diquat dibromide**
Journal	Saad_B, Ariffin_MM, Saleh_MI, (1997), 'Paraquat sensors containing membrane components of high lipophilicities Analytica Chimica Acta,' 338 (1-2), 89-96
Abstract	The development of high-performance paraquat selective potentiometric sensors based on octamethylcyclotetrasiloxane is described. In the fabrication of these sensors, the use of highly lipophilic PVC-based membrane components, namely, plasticizer and anionic sites, is emphasized. The electrochemical characteristics of such sensors were evaluated and compared with earlier paraquat ion-selective electrodes (ISEs) that were based on the same sensing compound but with nitrophenyl octyl ether (NPOE) as plasticizing solvent and also based on dibenzo-30-crown-10. The use of bis(1-butylpentyl)decane 1,1-diyldiglutarate (BBDG) and tetra-n-undecyl 3,3',4,4'-benzophenone tetracarboxilate (TBT) as plasticizer in conjunction with either sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NTB) or potassium tetrakis(4-chlorophenyl)borate (KTPB) as membrane additives all yielded functional paraquat selective chemical sensors of Nernstian slopes. Although the selectivity profile of these electrodes were slightly inferior as compared to a similar membrane system that uses NPOE as a plasticizer but was better than the earlier reported paraquat ISEs based on dibenzo-30-crown-10. A distinct advantage of the paraquat sensors described here was their resistance to fouling by surfactants as compared to earlier sensors that used NPOE as a plasticizer. The second part of this paper deals with the usage of the promising membrane systems described above when applied on the surface of platinum wire and subsequently used as a flow-through potentiometric detector. A brief description of the flow-through detector design and optimization of the flow-injection analysis (FIA) set-up were also presented. Analysis of 0.01-0.1 mM paraquat dichloride in backgrounds of well,river and lake waters when performed in the FIA mode gave excellent recoveries. A throughput of 85 samples/h

E.	**Diquat dibromide**
Journal	Ingram_JC, et al. , (1997), 'Direct surface analysis of pesticides on soil, leaves, grass, and stainless steel by static secondary ion mass spectrometry,' Environmental Science & Technology, 31(2), 402-408
Abstract	Direct surface analyses by static secondary ion mass spectrometry (SIMS) were performed far the following pesticides adsorbed on dandelion leaves, grass, soil, and stainless steel samples: alachlor, atrazine, captan, carbofuran, chlorthal-dimethyl, cypermethrin, 2,4-D, diuran,glyphosate, malathion, mocap, norflurazon, oxyfluorfen, paraquat temik, and trifluralin. The purpose of this study was to evaluate static SIMS as a tool for pesticide analysis, principally for use in screening samples for pesticides. The advantage of direct surface analysis compared with conventional pesticide analysis methods is the elimination of sample pretreatment including extraction, which streamlines the analysis substantially; total analysis time for SIMS analysis was ca. 10 min/sample. Detection of 16 of the 20 pesticides on all four substrates was achieved. Of the remaining four pesticides, only one (trifluralin) was not detected on any of the samples. The minimum detectable quantity was determined for paraquat on soil in order to evaluate the efficacy of using SIMS as a screening tool. Paraquat was detected at 3 pg/mm(2) (ca. 0.005 monolayers). The results of these studies suggest that SIMS is capable of direct surface detection of a range of pesticides, with low volatility, polar pesticides being the mast easily detected.

1999

F.	**Diquat dibromide**
Journal	Vermillion-Salsbury RL, Hercules DM, (1999), 'Analysis of diquat and paraquat by solid phase extraction directly coupled with matrix assisted laser desorption/ionization mass spectrometry,' *International Journal of Environmental Analytical Chemistry,* 73 (4): 297-308
Abstract	The herbicides diquat and paraquat have been successfully analyzed through a process which combines solid phase extraction (SPE) with Matrix Assisted Laser Desorption/Ionization (MALDI) mass spectrometry. Ion pair interactions are utilized to selectively load the herbicides onto a solid phase extraction disc. A MALDI matrix is then applied and analysis takes place directly from the disc, eliminating the need to elute the sample. This SPE-MALDI combination produced detection limits comparable to those obtained from conventional analysis with U.S. EPA Method 549.1. The SPE-MALDI method was tested on a variety of water samples and found to be suitable for "real world"

G.	**Diquat dibromide**
Journal	Sendra B, Panadero S, Gomez-Hens A, (1999), 'Selective kinetic determination of paraquat using long-wavelength fluorescence detection,' *Journal of Agricultural and Food Chemistry,*' 47 (9): 3733-3737
Abstract	The reaction between paraquat, ascorbic acid, and Cresyl Violet in alkaline medium and in the presence of sodium dodecyl sulfate has been applied for the first time to the development of a kinetic-fluorometric :method for the determination of paraquat. The reaction rate of this system is measured by using the stopped-flow mixing technique, which makes the method applicable to automatic routine analysis. Analytical data are obtained in similar to 30 s. The calibration graph is linear over the range 6-500 ng mL(-1), and the detection limit is 1.8 ng mL(-1). The relative standard deviation is <3%. The use of dynamic measurements at long wavelength favors the high selectivity of the method. Diquat behaves in this system similarly to paraquat, but its interferent effect is easily avoided by using cysteine. Th: proposed method has been applied to the determination of paraquat in tap water, milk, and white wine samples with recoveries of 89-104%.

H.	**Diquat dibromide**
Journal	Castro R, Moyano E, Galceran MT, (1999), 'Ion-pair liquid chromatography atmospheric pressure ionization mass spectrometry for the determination of quaternary ammonium herbicides,' Journal of Chromatography A, 830 (1): 145-154
Abstract	High-performance liquid chromatography coupled with atmospheric pressure ionization mass spectrometry (electrospray and atmospheric pressure chemical ionization) has been used to characterize some quaternary ammonium herbicides (quats). The separation of these compounds was carried out using ion-pair chromatography with heptafluorobutyric acid (15 mM, pH 3.3) and acetonitrile gradient elution for successful coupling to mass spectrometry. Detection limits down to 0.1-4 mu g l(-1) were obtained for spiked tap water following a preconcentration step. Good reproducibilities (day-to-day and run-to-run) were also obtained.

I.	**Diquat dibromide**
Journal	Lazar IM, Lee ML, (1999) ,'Capillary electrophoresis time-of-flight mass spectrometry of paraquat and diquat herbicides,' *Journal of Microcolumn Separations*, 11 (2): 117-123
Abstract	Capillary electrophoresis (CE) and mass spectrometry (MS) were investigated for the analysis of paraquat and diquat herbicides. The mass spectrometer was a home-built time-of-flight instrument (TOFMS) equipped with an electrospray ionization (ESI) source. A coaxial liquid sheath ESI source was utilized for interfacing the CE to the TOFMS, and mass spectra were acquired with both liquid sheath and microspray sources. The ESI-TOF spectra of paraquat and diquat were dependent on the background electrolyte composition; singly or doubly charged ions were displayed preferentially. Volatile buffer systems, compatible with the ESI-MS, were used in mixed aqueous/organic solvents. By using the sample stacking technique at the CE injection port, low femtomole detection was achieved from 5 mu M solutions.

2000

J.	**Diquat dibromide**
Journal	Carneiro MC, Puignou L, Galceran MT (2000), 'Comparison of silica and porous graphitic carbon as solid-phase extraction materials for the analysis of cationic herbicides in water by liquid chromatography and capillary electrophoresis,' *Analytica Chimica Acta*, 408 (1-2): 263-269
Abstract	Preconcentration methods for the analysis of paraquat (PQ), diquat (DQ) and difenzoquat (DF) in water samples by solid-phase extraction (SPE) with silica and porous graphitic carbon (PGC) were evaluated. The breakthrough volumes of three quaternary ammonium herbicides were calculated in order to compare the loading capacity of both sorbents. They were determined by capillary electrophoresis (CE) and ion-pair reversed-phase liquid chromatography (LC) with UV detection. The recoveries were determined by spiking tap and river waters. Although the data showed that both sorbents were able to preconcentrate the cationic herbicides using CE and LC as separation and quantification techniques, silica was inappropriate for the CE determination of DF because marked distortions in the base line occurred. The best results were obtained for PGC with both separation techniques, which gave recoveries ranging from 65 to 90% and standard deviations between 4 and 10%. Practical detection limits (LODs) with LC were about 0.2 mu g l(-1) and were one order of magnitude higher with CE.

2001

K.	**Diquat dibromide**
Journal	Mallat E, et al., (2001), 'Fast determination of paraquat residues in water by an optical immunosensor and validation using capillary electrophoresis-ultraviolet detection,' *Analytica Chimica Acta*, 427 (2): 165-171
Abstract	A solid-phase fluoroimmunoassay combined with an optical transducer chemically modified with an analyte derivative coupled to a FIA system was used [A. Brecht, A. Klotz, C. Barzen, G. Gauglitz, R. Harris, G. Quigley, J. Wilkinson, P. Sztajnbok, R. Abuknesha, J. Gascon, A. Oubina, D. Barcelo, Anal. Chim. Acta 362 (1998) 69]. Excitation and collection of fluorescence from fluorescently labelled anti-paraquat antibodies locally bound at the planar interface allows the measurement of the fluorescent signal which is indirectly related to the paraquat concentration of the sample. Matrix effects on the immunosensor response were observed, thus leading to the following detection limits, 0.01 and 0.06 mug l(-1), when analyzing paraquat in MilliQ and in river water, respectively, The validation of the biosensor was carried out analyzing paraquat samples by capillary zone electrophoresis with ultraviolet detection (CZE-UV) at 214 nm. Preconcentration of the samples prior to their injection in the capillary electrophoresis were performed using the automated solid-phase extraction system (ASPEC-XL). Paraquat samples were adjusted at pH 9 and were percolated through a silica cartridge, subsequent elution was carried out using a mixture of hydrochloric acid and methanol and afterwards samples were evaporated and injected.

L.	**Diquat dibromide**
Journal	Evans CS, Startin JR, Goodall DM, Keely BJ, (2001), 'Tandem mass spectrometric analysis of quaternary ammonium pesticides' *Rapid Communications in Mass Spectrometry*, 15 (9): 699-707
Abstract	A detailed MSn study on an ion trap instrument of the quaternary ammonium pesticides paraquat, diquat, difenzoquat, mepiquat and chlormequat reveals a number of ions not reported previously, and has allowed examination of the fragmentation pathways. A number of transitions that are highly specific to each quat have been identified. Optimal ion trap operating conditions determined using Simplex optimisation can promote either detection of a particular fragmentation transition or a range of MS/MS product ions with a high overall signal response. Thus, fragmentation conditions were optimised to enhance the specificity or sensitivity of MS/MS methods.

M.	**Diquat dibromide**
Journal	Cheng Y, Hercules DM, 2001, 'Studies of pesticides by collision-induced dissociation, postsource-decay, matrix-assisted laser desorption/ionization time of flight mass spectrometry,' *Journal of the American Society for Mass Spectrometry*, 12 (5): 590-598
Abstract	The use of collision-induced dissociation, postsource decay (CID-PSD) matrix-assisted laser desorption/ionization (MALDI) mass spectrometry for the analysis of small organic molecules is demonstrated. Three pesticides: paraquat, diquat, and difenzoquat were chosen for this study. The matrices 2,5-dihydroxybenzoic acid (DHB), alpha -cyano-4-hydroxycinnamic acid (alpha -CHCA), and sinapinic acid (SA) were selected to investigate the effect of the matrix on the CID-PSD MALDI spectra of these molecules. alpha -CHCA and DHB were found to be appropriate matrices for the pesticides studied. Spectra for a given pesticide obtained from different matrices were compared with each other, and the differences between them are discussed. A comparison of CID-PSD MALDI with fast-atom bombardment MS/MS spectra is presented; the agreement of pesticide fragmentation patterns between the two methods indicates that CID-PSD MALDI MS is a reliable and efficient technique for structural elucidation of small molecules.

N.	**Diquat dibromide**
Journal	Castro R, Moyano E, Galceran MT, (2001) 'Determination of quaternary ammonium pesticides by liquid chromatography-electrospray tandem mass spectrometry,' *Journal of Chromatography A*, 914 (1-2): 111-121
Abstract	A method for the direct determination of paraquat, diquat, chlormequat and difenzoquat in water samples, using an on-line solid-phase extraction-liquid chromatography-tandem mass spectrometry system was developed. No sample preparation was required and the detection limits were below the European Union maximum residue levels. The chromatographic separation was performed using an XTera MS C-8 column. The concentration of the ion pair reagent, the pH and the gradient elution were optimized to give high recoveries and good chromatographic resolution between quats. The detection was carried out using an ion trap as mass analyzer. Parameters such as the magnitude and duration of the resonant excitation voltage and the magnitude of the trapping RF voltage for full scan tandem mass spectrometry (MS-MS) experiments were studied to establish the optimal experimental conditions. Moreover, the accurate optimization of these parameters allowed MS-MS experiments of low mass ions, below m/z 200, providing unambiguous peak identification. Finally, the reproducibility of the proposed method was shown by good run-to-run and day-to-day precision values and its applicability to the determination of quats in drinking water was evaluated using spiked samples.

O.	**Diquat dibromide**
Journal	Castro R, Moyano E, Galceran MT, (2001), 'Ion-trap versus quadrupole for analysis of quaternary ammonium herbicides by LC-MS,' *Chromatographia*, 53 (5-6): 273-278
Abstract	An ion-trap mass spectrometer for determination of quaternary ammonium herbicides in water samples is evaluated. Implementation oi the method previously optimized in a quadrupole mass spectrometer (VG Platform ii) in an ion-trap (LCQ) required modifications to the sample inlet of the electrospray source. Quality parameters were established and detection limits, after trace enrichment, ranged 5 - 50 ng L-1. Good reproducibilities (day-io-day and run-to-run) < 12% were obtained. The method was applied to analysis of spiked samples and the results were comparable with those determined using a quadrupole mass spectrometer.

2002

P.	**Diquat dibromide**
Journal	Nunez O, Moyano E, Galceran MT, (2002), 'Solid-phase extraction and sample stacking-capillary electrophoresis for the determination of quaternary ammonium herbicides in drinking water,' *Journal of Chromatography A*, 946 (1-2): 275-282
Abstract	Conditions for the simultaneous determination of paraquat, diquat and difenzoquat by capillary zone electrophoresis were established by combining two preconcentration procedures. Off-line solid-phase extraction was used for the isolation and preconcentration of quats in drinking water. Quats were then analysed by capillary electrophoresis using sample stacking with matrix removal as on-column preconcentration procedure. Two different porous graphitic carbon cartridges were compared. The breakthrough volumes of the three herbicides were calculated and the loading capacity of the sorbents was compared. Recoveries higher than 80% for difenzoquat and around 40% for paraquat and diquat were obtained when a sample volume of 250 ml was percolated. For the stacking-capillary electrophoresis analysis of quats, 50 mM acetic acid-ammonium acetate (pH 4.0), 0.8 mM CTAB with 5% (v/v) methanol as carrier electrolyte was used. Detection limits, based on a signal-to-noise ratio of 3:1, were lower than 0.3 mug/l for standards in Milli-Q water, and lower than 2.2 mug/l for drinking water samples. Run-to-run and day-to-day precision were established. The two preconcentration procedures used together was successfully applied to the analysis of the three herbicides in spiked drinking water at concentrations below the max. admissible EPA levels.

1998

1.	**p-octylphenol**
Journal	Sun C, Baird M (1998), 'The determination of alkyl phenol ethoxylates in wool-scouring effluent,' *Journal of the Textile Institute,* 89 (4): 677-685 Part 1
Abstract	Alkyl phenol ethoxylates (APEOs), particularly nonyl phenol ethoxylates (NPEOs), are non-ionic surfactant components used in woollen-yam spinning oils and industrial detergents. In recent years, concern over the hormone-disrupting properties of NPEOs has given rise to proposals to ban their use in EU countries. A sensitive and reliable method of detecting NPEOs on incoming raw material and in textile effluent is therefore required. A method has been developed to detect NPEOs at ppm levels in wool-scouring effluent by the application of extraction and clean-up procedures followed by high-performance-liquid-chromatography (HPLC) analysis

2.	**p-octylphenol**
Journal	Alexander JN, Schultz GA, Poli JB (1998), 'Development of a nano-electrospray mass spectrometry source for nanoscale liquid chromatography and sheathless capillary electrophoresis,' *Rapid Communications in Mass Spectrometry,* 12 (17): 1187-1191
Abstract	A Fisons Quattro I electrospray ionization (ESI) source has been modified to produce stable electrospray ion currents at flow rates as low as 50 nL/min, The original counter electrode and skimmer cone lens of the Fisons ESI source have been replaced with a spherical cone lens. This improved source provides a greater range of x,y,z positioning of a stainless steel tip resulting in a stable ion signal for flow rates of 50 nL/min to 2 mu L/min, A tapered stainless steel electrospray tip (50 mu m i,d,) was evaluated for mass spectrometry using nano-liquid chromatography (50 pm i,d,, flow rate = 120 nL/min) and sheathless capillary electrophoresis, The analysis of a nonionic surfactant, octylphenol ethoxylate, was accomplished with both nanoscale separation techniques.

3.	**p-octylphenol**
Journal	Bennett_ER, Metcalfe_CD, (1998) ‘Distribution of alkylphenol compounds in great lakes sediments, United States and Canada,’ *Environmental Toxicology and Chemistry*, 17(7), 1230-1235
Abstract	Alkylphenol polyethoxylates are a major class of nonionic surfactants that are microbially degraded in sewage treatment plants (STPs) and sediments to more toxic and hydrophobic alkylphenols. Recent data on the estrogenic activity of alkylphenols has prompted interest in the distribution of these compounds in the aquatic environment. Sediment samples were collected from several sites (n = 28) at industrialized and pristine regions of Lake Huron, Lake Erie, and Lake Ontario, USA and Canada, and analyzed for concentrations of 4-nonylphenol (NP) and 4-(tert)-octylphenol (OP). Also, sludge samples were taken from a secondary STP in Whitby, Ontario, Canada, Sediment and sludge samples and analytical standards were prepared for analysis by gas chromatography-mass spectrometry in selected ion mode by combined acetylation and supercritical fluid extraction. Concentrations of NP were up to 37 mu g/g in sediments and >300 mu g/g in the sewage sludge. Concentrations of OP were up to 23 mu g/g in sediment and 21 mu g/g in the sewage sludge. These data indicate that alkylphenols are distributed widely in sediments in the lower Great Lakes. However, concentrations of NP were present at high (mu g/g) levels only in sediments near urban and industrialized centers.

1999

4.	**p-octylphenol**
Journal	Lee HB (1999), 'Review of analytical methods for the determination of nonylphenol and related compounds in environmental samples,' *Water Quality Research Journal of Canada,* 34 (1): 3-35
Abstract	Analytical methods published in the last 20 years for the extraction, chromatographic separation, and quantification of alkylphenol ethoxylates (APEO) and related compounds in environmental samples are reviewed. Examples of various isolation and pre-concentration techniques for water, effluent, sediment and sludge are presented. This includes procedures from the classical liquid-liquid and Soxhlet extraction to the up-to-date solid phase and supercritical fluid extraction. Chromatographic separation of APEO by normal and reversed phase liquid chromatography (LC) and capillary column gas chromatography (GC) is compared. A variety of quantification methods involving the common LC and GC detectors as well as various mass spectrometric techniques are also discussed.

2000

5.	**p-octylphenol**
Journal	Barber LB, Brown GK, Zaugg SD (2000), 'Potential endocrine disrupting organic chemicals in treated municipal wastewater and river water.' *Analysis Of Environmental Endocrine Disruptors, ACS Symposium Series*, 747: 97-123
Abstract	Select endocrine disrupting organic chemicals were measured in treated wastewater from Chicago, IL, Minneapolis/St. Paul, MN, Detroit, MI, and Milwaukee, WI, and in the Des Plaines, Illinois, and Minnesota Rivers during the fall of 1997 and the spring of 1998. Emphasis was given to alkylphenol-polyethoxylate (Contaminants were isolated by continuous liquid-liquid extraction (CLLE) with methylene chloride and analyzed by gas chromatography/mass spectrometry in full scan and selected ion monitoring modes. The extracts were derivatized to form the methyl esters of alkylphenolethoxycarboxylates (APEC), and EDTA was isolated by evaporation and derivatized to form the tetrapropyl ester. The mass spectra of nonylphenol (NP) and octylphenol (OP) compounds are complex and show variations among the different ethoxylate and carboxylate homologs, reflecting variations in the ethylene oxide chain length. Recoveries for target compounds and surrogate standards ranged from 20-130%, with relative standard deviations of 9.9-53%. Detection limits for the various compounds ranged from 0.06-0.35 mug/L. Analysis of the wastewater effluents detected a number of compounds including NP, NPEO, OP, OPEO, NPEC, caffeine, and EDTA at concentrations ranging from <1-439 mug/L, with EDTA and NPEC being most abundant. There was variability in compound distributions and concentrations between the various sewage treatment plants, indicating differences in treatment type and influent composition. Several wastewater-derived compounds were detected in the river samples, with EDTA and NPEC persisting for considerable distance downstream from wastewater discharges, and NP and NPEO being attenuated more rapidly.

6.	**p-octylphenol**
Journal	Chiron S, Sauvard E, Jeannot R (2000), 'Determination of nonionic polyethoxylate surfactants in wastewater and sludge samples of sewage treatment plants by liquid chromatography-mass spectrometry,' *Analusis*, 28 (6): 535-542
Abstract	An analytical method is proposed in order to determine the major nonionic surfactants, octylphenolpolyethoxylates (OPEOs), nonylphenolpolyethoxylates (NPEOs) and aliphatic alcoholpolyethoxylates (AEOs), and their metabolites, nonylphenol and octylphenol in wastewater and sludge samples of sewage treatment plants. This method involved a Soxtec extraction step and a solid phase extraction step for the nonionic surfactant extraction from sludge and wastewater samples, respectively. With both methodologies, all recovery values were higher than 70 %. Quantitation and identification of individual compound were carried out by liquid chromatography-mass spectrometry (LC/MS) using electrospray (ESP) as ionization mode. Reverse phase LC chromatography allowed the elution of all oligomer constituents of each homolog component into a single peak. Gathering all the oligomers into a single peak increased the peak intensity and provided a way to determine low concentration of APEOs and AEOs in different environmental matrices. Information on the oligomers distribution of APEOs and AEOs could be obtained by the extraction of selected m/z ions from the TIC chromatograms. Positive ESP LC/MS analyses of AEOs and APEOs yielded primary pseudo-molecular ions of the [M + Na](+) type for each oligomer. The negative ionization mode allowed the determination of the two metabolites, nonylphenol and octylphenol, characterized by the pseudo molecular [M-H](-) ion. Limits of detection achieved were 0.1 mug/L in wastewater sample and 10 ng/g in sludge samples. The developed LC-ESP/MS method was applied to the analysis of wastewater and sludge samples of two sewage treatment plants located in Orleans (France).

7.	**p-octylphenol**
Journal	Petrovic M, Barcelo D (2000), 'Determination of anionic and nonionic surfactants, their degradation products, and endocrine-disrupting compounds in sewage sludge by liquid chromatography/mass spectrometry,' *Analytical Chemistry*, 72 (19): 4560-4567
Abstract	A comprehensive analytical method based on reversed-phase liquid chromatography and mass spectrometry using both atmospheric pressure chemical ionization and electrospray ionization has been developed for the simultaneous determination of anionic and nonionic surfactants, their polar degradation products, and endocrine-disrupting compounds (EDCs) in sewage sludge; Extraction of target compounds, with recovery rates from 86% to nearly 100% for polyethoxylates and from 84 to 94% for polar degradation products, was achieved applying ultrasonic solvent extraction with a mixture of methanol/dichloromethane (7:3, v/v), Cleanup of sample extracts was performed on octadecyl solid-phase extraction cartridges. Determination of less polar compounds: alcohol ethoxylates (AEOs), nonylphenol ethoxylates (NPEOs), coconut diethanol amides, poly(ethylene glycol)s, and phthalate esters was accomplished by reversed-phase LC-APCI-MS in positive ionization mode, while more polar compounds: nonylphenolcarboxylates, nonylphenol (NP), octylphenol, and bisphenol A were analyzed by ion-pair LC-ESI-MS under negative ionization conditions. This protocol was successfully applied to the trace determination of anionic and nonionic surfactants, polar degradation products, and EDCs in sewage sludge collected from different sewage treatment plants, The analysis revealed the presence of NP at high concentration levels ranging from 25 to 600 mg/kg, Polyethoxylates (AEOs and NPEOs) were also found in all samples at parts-per-million levels (10-190 mg/kg AEOs and 2-135 mg/kg NPEOs, respectively).

8.	**p-octylphenol**
Journal	Ferguson PL, Iden CR, Brownawell BJ (2000), Analysis of alkylphenol ethoxylate metabolites in the aquatic environment using liquid chromatography-electrospray mass spectrometry, *Analytical Chemistry*, 72 (18): 4322-4330
Abstract	A quantitative method is described for the analysis of the metabolites of alkylphenol ethoxylate (APEO) surfactants in estuarine water and sediment samples using reversed-phase high-performance liquid chromatography with electrospray mass spectrometry detection. Nonyl- and octylphenols, nonyl- and octylphenol mono-, di-, and triethoxylates, halogenated nonylphenols, and nonylphenol ethoxycarboxylates were concentrated from water samples using a C-18 solid-phase extraction procedure. A novel, continuous-non., high-temperature, sonicated extraction system was developed to isolate APEO metabolites from sediment samples. Quantitative LC-MS was performed in the negative ion mode for nonylphenols, octylphenols, and halogenated nonylphenols and in the positive ion mode for nonyl- and octylphenol ethoxylates using selected ion monitoring with isotopically labeled surrogate standards. Recoveries for sediment and water analyses ranged between 78 and 94%, and detection limits for APEO metabolites were between 1 and 20 pg injected on column. This is a significant improvement over previously reported methods. Suppression of analyte response was encountered in the presence of matrix components in sediment samples, but this effect was eliminated by careful selection of surrogate and internal standards. Individual APEO metabolite concentrations of 1-320 ng/L and 5-2000 ng/g are reported for water and sediment samples, respectively, from Jamiaca Bag, NY.

9.	**p-octylphenol**
Journal	Mol HGJ, Sunarto S, Steijger OM (2000), 'Determination of endocrine disruptors in water after derivatization with N-methyl-N-(tert.-butyldimethyltrifluoroacetamide) using gas chromatography with mass spectrometric detection,' *Journal of Chromatography A*, 879 (1): 97-112
Abstract	The combined gas chromatographic determination of a number of hydroxyl-group containing endocrine disrupters, including 4-octylphenol, 4-nonylphenol, 2,4-dichlorophenol, pentachlorophenol, 4-tert.-butylbenzoic acid, bisphenol-A, 17 beta-estradiol and 17 alpha-ethynylestradiol, was investigated. Derivatization, required for sensitive determination of these compounds, was carried out using N-methyl-N-(tert.-butyldimethyltrifluoroacetamide). A number of parameters affecting the derivatization reaction, like temperature, time, matrix, solvent, and amount of reagent were studied in detail. Quantitative yields were obtained for real-life extracts after optimization, but the hormones were only mono-substituted. Both solid-phase extraction (SPE) and liquid-liquid extraction were studied as extraction methods, with emphasis on SPE material and effect of pH. Recoveries and RSD for analysis of surface water samples were 58-106 and 6-16% (n=4), respectively, when using SPE, and 109-117 and 6-14% (n=6) when using Liquid-liquid extraction. The method developed allows routine analysis of surface water for traces of endocrine disrupters. The limits of detection of were 4-6 ng/l but higher for the hormones.

2001

10.	**p-octylphenol**
Journal	Smith E, Ridgway I, Coffey M (2001), 'The determination of alkylphenols in aqueous samples from the Forth Estuary by SPE-HPLC-fluorescence,' *Journal of Environmental Monitoring*, 3 (6): 616-620
Abstract	Nonylphenol and octylphenol have been identified as endocrine disrupters with the ability to cause reproductive deformities in a number of organisms. A normal phase high-performance liquid chromatography (HPLC) method with fluorescence detection wets developed with a mobile phase of cyclohexane/methyl-tertiary-butyl ether (MTBE) (70+30). The extraction of the alkylphenols from the water samples wets evaluated using solid-phase extraction (SPE) with a C-2 packing sorbent. The complete method was validated and the limit of detection calculated to be 0.15 ppb (mug l(-1)). The method was novel for the analysis of specific alkylphenols in an aqueous matrix. A surrey of the Forth Estuary in May 2000 resulted in no detectable amounts of nonyl- or octylphenol, whilst a survey during August of the same year produced concentrations ranging from 0.17-1.90 ppb for nonylphenol and 0.17-1.38 ppb for octylphenol. These results are compared with other river and estuarine studies with concentrations considered in terms of toxicity to aquatic organisms. The concentrations determined in the Forth Estuary are consistent with a contaminated though not grossly polluted estuarine system.

11.	**p-octylphenol**
Journal	Staples CA, Naylor CG, Williams JB, Gledhill WE (2001), 'Ultimate biodegradation of alkylphenol ethoxylate surfactants and their biodegradation intermediates,' *Environmental Toxicology and Chemistry*, 20 (11): 2450-2455
Abstract	The ultimate biodegradation of the commercial products nonylphenol ethoxylates (NPE9), octylphenol ethoxylates (OPE9), and their biodegradation intermediates, NPE1.5, OPE1.5, NP, and OP, was measured using conventional methods. The extent of biodegradation was also determined by gas chromatography/mass spectrometry (GC/MS) and high-performance liquid chromatography (HPLC) analysis of metabolites and measurement of dissolved organic carbon. Optimized pseudo-first order degradation rate constants and half-lives were calculated from these data and from previously published data, using Larson's equation for surfactant degradation kinetics. Ultimate aerobic biodegradation of alkylphenol ethoxylates and their biodegradation intermediates has now been examined using acclimated wastewater treatment plant sludge as the microbial seed, household wastewater treatment systems. and unacclimated fresh water, seawater, and soil. Ultimate biodegradation half-lives ranged from about one to four weeks and provide definitive evidence for the extensive biodegradability of alkyphenol ethoxylates (APE) surfactants and their metabolites and their lack of persistence in the environment.

12.	**p-octylphenol**
Journal	Careri M, Elviri L, Mangia A (2001) ,'Development and validation of a method using on-line solid-phase extraction and liquid chromatography with ultraviolet detection for the determination of bisphenol A, octylphenol, and nonylphenol in groundwater,' *Journal of AOAC International*, 84 (5): 1383-1392
Abstract	Alkylphenols are non biodegradable metabolites arising from various pathways of aerobic and anaerobic degradation of the nonionic surfactants alkylphenol ethoxylates. A method based on the use of on-line solid-phase extraction (SPE) and liquid chromatography (LC) with UV detection was developed to determine bisphenol A, octylphenol, and nonylphenol at trace levels in water. The on-line coupled SPE procedure automatically enables an approximately 300-fold preconcentration of analytes, which can be further enhanced by an increase in applied sample volume. By using C-18 cartridges, recoveries of > 90% were obtained for all the analytes. A validation procedure was carried out with a groundwater sample to ensure the quality of the results; performance criteria such as detection limits (LODs), quantitation limits (LOQs), linearity, and precision were evaluated. LODs and LOQS in the range of 0.17-0.36 and 0.35-1.88 mug/L, respectively, were found; for all the analytes, linearity was established over 2 orders of magnitude (r^2 > 0.997, n = 54). The intraday repeatability values expressed as relative standard deviations were <5.3%; a nested analysis of variance was performed to verify the influence of 3 different factors, i.e., different days, extraction procedure, and LC replicate injection, on data precision.

13.	p-octylphenol
Journal	Benomar SH, Clench MR, Allen DW (2001), 'The analysis of alkylphenol ethoxysulphonate surfactants by high-performance liquid chromatography, liquid chromatography-electro spray ionisation-mass spectrometry and matrix-assisted laser desorption ionisation-mass spectrometry,' *Analytica Chimica Acta*, 445 (2): 255-267
Abstract	Commercial nonylphenol ethoxysulphonate and octylphenol ethoxysulphonate surfactant formulations, used for enhanced oil recovery, have been analysed by high-performance liquid chromatography (LC), liquid chromatography-electrospray ionisation-mass spectrometry (LC-ESI-MS) and matrix-assisted laser desorption ionisation-mass spectrometry (MALDI-MS). Mixed-mode Cl8/SAX and C8/SAX columns were used for both liquid chromatography and liquid chromatography-mass spectrometry analyses. Matrix-assisted laser desorption ionisation-mass spectra were obtained using either alpha -cyano-4-hydroxycinnamic acid or 2,5-dihydroxybenzoic acid as matrix with the addition of lithium chloride to simplify the mass spectra obtained. Data obtained from each method indicate that the nonylphenol ethoxysulphonate, formulation has an ethoxymer (EO) chain length ranging from 2 to 13 EO units with an average of 6.26. This is in broad agreement with earlier studies, although the range was reported as 2-15. However, the data obtained suggest that the octylphenol ethoxysulphonate formulation has an ethoxymer chain length ranging from 1 to 8 EO units with an average chain length of 3.67. This is in contrast to earlier studies carried out by LC only, which suggested that the chain length ranged from 2 to 6 EO units with an average of 3.6. A method for the extraction of alkylphenol ethoxysulphonates from sea water using graphitised carbon black solid-phase extraction cartridges has also been developed.

14.	p-octylphenol
Journal	Kuch HM, Ballschmiter K (2001), 'Determination of endocrine-disrupting phenolic compounds and estrogens in surface and drinking water by HRGC-(NCI)-MS in the picogram per liter range,' *Environmental Science & Technology*, 35 (15): 3201-3206
Abstract	Analysis of phenolic estrogenic active compounds in surface and drinking water at pg/l. Water samples from 1 to 5 L were extracted by solid-phase extraction (SPE) on a cartridge system containing LiChrolut EN as sorbent. Phenols and steroids were converted into their pentafluorobenzoylate esters in an extractive derivatization reaction. The derivatives were then determined by high-resolution gas chromatography with negative chemical ionization mass spectrometric detection (HRGC-(NCl)-MS) in the selected ion mode (SIM). All results were also confirmed by HRGC with electron capture detection (ECD). This highly sensitive and specific method gives a limit of detection (LOD) of 20 pg/L for bisphenol A and 4-tert-octylphenol in drinking water samples and 50 pg/L in STW effluent, respectively. The LODs for technical 4-nonylphenol, 17a-ethinylestradiol, and other estrogens are in the range of 50 pg/L in drinking water to 200 pg/L in STW effluent, respectively. In all river water samples in southern Germany, bisphenol A was found in concentrations ranging from 500 pg/L up to 16 ng/L, 4-nonylphenol was from 6 up to 135 ng/L, and the steroids were from 200 pg/L up to 5 ng/L. In drinking water, bisphenol A was found in concentrations ranging from 300 pg/L to 2 ng/L, 4-nonylphenol was from 2 to 15 ng/L, 4-tert-octylphenol was from 150 pg/L to 5 ng/L, and the steroids were from 100 pg/L to 2 ng/L. Mean recoveries over the whole analytical protocol, measured in bidistilled water, generally exceeded 70%. These results indicate that environmental endocrine-disrupting estrogens are not completely removed in the process of sewage treatment but are carried over into the general aquatic environment. After ground passage, they can eventually be found in drinking water.

15.	p-octylphenol
Journal	Cathum S, Sabik H (2001), 'Simultaneous determination of alkylphenol polyethoxylate surfactants and their degradation products in water, effluent and mussel using gas chromatography-mass spectrometry,' *Chromatographia*, 53: S400-S405 Part 2 Suppl. S 2001
Abstract	Alkylphenol polyethoxylate surfactants (APnEO) are used in many industrial, commercial and household applications. Their widespread use has raised public concern about these chemicals and their degradation products in rivers and waterways. A gas chromatography-mass spectrometry (GC-MS) method was developed to determine 4-nonylphenol, 4-tert-octylphenol, alkylphenol polyethoxylates (n = 1-16), nonylphenolmonoethoxycarboxylic acid and octylphenolmonoethoxycarboxylic acid in surface water, effluent, and mussels. The method is based on the derivatization of analytes with pentafluorobenzyl bromide (PFB-Br), followed by chromatography cleanup and GC-MS determinations. Method detection limits were in the range of 1 ng/L for surface water and effluent, and 3 ng/g for mussel samples. Recovery of target compounds ranged from 40-102% and 24-111% in water and mussel samples, respectively. Several non-ionic surfactants were detected at concentrations ranging from 0.009 to 10.324 mug/L in the St. Lawrence River (surface water and sewage effluent) and at 177 to 12440 ng/g in mussels, introduced in this river for 62 days.

2002

16.	p-octylphenol
Journal	Petrovic M et al. (2002), 'Occurrence and distribution of nonionic surfactants, their degradation products, and linear alkylbenzene sulfonates in coastal waters and sediments in Spain,' *Environmental Toxicology and Chemistry*, 21 (1): 37-46
Abstract	Spain is one of the European countries that still discharges untreated wastewaters and sewage sludge to the sea. A total of 35 samples of coastal waters and 39 samples of harbor sediments was analyzed. Samples were collected from several hot spots on the Spanish coast, such as the harbors of Tarragona, Almeria, and Barcelona, the mouths of the Besos and Llobregat rivers, the Bay of Cadiz, and various yacht harbors at the Mediterranean coast. A generic analytical procedure based on solid-phase extraction-liquid chromatography-atmospheric pressure chemical ionization / electrospray ionization mass spectrometry (SPE-LC-APCI/ESI-MS) was employed for determining the concentrations of alcohol ethoxylates (AEO), nonylphenol ethoxylates (NPEO), coconut diethanol amides (CDEA), nonylphenoxy-monocarboxylates (NPEC), nonylphenol (NP), octylphenol (OP), and linear alkylbenzene sulfonates (LAS) in sediment and water samples. The analysis revealed the presence of considerably high concentrations of NPEOs and NP near the points of discharge of industrial and urban wastewaters. Nonylphenol was found in 47% of water samples and in 77% of all sediment samples analyzed. Values for NP ranged from <0.15 to 4.1 <mu>g/L in seawater and from <8 to 1,050 <mu>g/kg in sediments. Levels of AEOs and CDEAs in seawater and marine sediments are reported for the first time. Concentrations of CDEAs in sediment, which were predominated by C-11 through C-15 homologues, ranged from 30 to 2,700 mug/kg, while in seawater, concentrations found were up to 24 mug/L. The AEOs were found to accumulate in a bottom sediment and they were detected in all analyzed sediment samples in concentrations from 37 to 1,300 mug/kg.

Environmental Analysis (3)

Diquat dibromide and *p*-octylphenol have the potential to cause short-term and long-term damage to the environment. Therefore, it is important to consider the measurement of the concentrations of chemicals immediately after the incident and their subsequent fate. The majority of the chemicals were discharged into the environment via the drains on the site and then into the beck.

Discuss in your groups:

- The type, frequency and number samples that would be required.
- Those who could be prosecuted for the escape of pollutants into the River Dribble. Give your reasoning.
- Those who would be liable to pay for the monitoring of the pollution and subsequent clean up operations.

Assume that a monitoring programme is being set up for this river system. Your task is to produce recommendations for the implementation of the monitoring programme.

- Outline analytical methods that could be used to detect diquat dibromide and *p*-octylphenol based on the references provided.

Notes

Diquat dibromide (1997-2002)

1. Galceran_MT, Carneiro_MC, Diez_M, Puignou_L, (1997) ‘Separation of quaternary ammonium herbicides by capillary electrophoresis with indirect uv detection,’ Journal of Chromatography A, 782(2), 289-295

2. Walker_PA, Shaver_JM, Morris_MD, (1997), ‘Identification of cationic herbicides in deionized water, municipal tap water, and river water by capillary isota-chophoresis / on-line raman spectroscopy,’ Applied Spectroscopy, 51(9), 1394-1399

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Environmental Analysis (4)

Diquat dibromide and *p*-octylphenol have the potential to cause short-term and long-term damage to the environment. Therefore, it is important to consider the measurement of the chemicals immediately after the incident and their subsequent fate. The majority of the chemicals were discharged into the environment via the drains on the site and then into the beck.

Discuss in your groups:

- The type, frequency and number samples that would be required.
- Those who could be prosecuted for the escape of pollutants into the River Dribble. Give your reasoning.
- Those who would be liable to pay for the monitoring of the pollution and subsequent clean up operations.

Assume that a monitoring program is being set up for this river system. Your task is to produce recommendations for the implementation of the monitoring programme.

- Outline analytical methods that could be used to detect diquat dibromide and *p*-octylphenol based on the application reviews in Analytical Chemistry that appear on the 15 June edition in odd years.

Review of Environmental Analysis (1991 - 2001)

Clement RE, Yang PW, Koester CJ, (2001), ‘Environmental analysis,’ *Analytical Chemistry*, 73 (12): 2761-2790

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Richardson SD, (2001), ‘Water analysis,’, *Analytical Chemistry*, 73 (12): 2719-2734

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Memo

20th May
To Investigation Team

Following the warehouse fire of 19 May, diquat dibromide, and *p*-octylphenol are believed to be present in the River Dribble. The Environment Department of Midshire County Council requires you to implement the following programme. Samples should be taken from the 20 May initially each day for the first fourteen days followed by monitoring once a week for the subsequent six weeks for diquat dibromide and p-octylphenol. Following this eight-week monitoring period, a monthly check (every 30 days) will be made for an indefinite period on the levels of *p*-octylphenol in both water and sediment samples until such time as the levels have dropped below the maximum permitted concentrations.

You are instructed to commission a sampling and analysis programme from the details of the companies attached to this memo. You may choose any combination of companies for any service in order to obtain the lowest cost within the constraints outlined below:

- 12 filtered water samples and 9 sediment samples will be taken from three sampling sites.
- Results should be returned within 7 days for diquat dibromide and 28 days for *p*-octylphenol.
- Sediment samples are not required for diquat dibromide analysis.
- All companies employed must have the relevant analytical techniques NAMAS or UKAS accredited.

Please find enclosed the the brochures for Wartanal, STS, Pork and Gaskett, and Strudenfarter. A briefing paper, completed analysis request form, blank analysis request form, costings sheet and year planner are also attached. It has been calculated that it would cost about £200,000 for the Environmental Department to perform this analysis ‘in house’. This may be achieved more economically by contracting the work out to private companies.

Yours truly,

SMarshall

Mr. Simon Marshall
Director of the Environmental Department

Notes

The budget must include costings for collection of samples and transport. This may be performed ‘in house’ or as part of a package, which may be provided by any of the nominated companies. It has been

Costing of sample collection per collection date	
Total sampling time per visit	8 hours
Cost per hour	£15.00
Disposables	£14.00
Transport cost per sampling visit	£24.00

You may only budget up to the end of the year. One of the nominated companies is based in Germany. The current exchange rate, £/Euro is 0.89. Each conversion attracts a 2% commission by the exchanging bank.

The required detection limits are as follows:-

Detection Limits required	Sediment	Water
Diquat dibromide	N/A	$0.1\ \mu g\ l^{-1}$
p-octylphenol	$1.4\ ng\ g^{-1}$	$1.0\ \mu g\ l^{-1}$

The Task

Use the following information to decide who should carry out the sampling and the analysis programme.

When you have made your decision you will be required to give a 10-minute presentation justifying **all** your decisions. An executive summary of your proposals (2 x A4) needs to be submitted by the date given by the tutor.

The report should include:-

- Summary of companies reviewed
- Summary of costs
- Factors considered
- Executive summary of decisions including justification

Year Planner

	T	W	T	F	S	S	M	T	W	T	F	S	S	M	T	W	T	F	S	S	M	T	W	T	F	S	S	M	T	W	T	F	S	S	M	T
Jan			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31			
Feb						1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28			
Mar						1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
Apr		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30					
May				1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31		
Jun							1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
Jul		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31				
Aug					1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	
Sep	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30						
Oct			1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31			
Nov						1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	
Dec	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31					

Pork & Gaskett Analytical Services

Pork & Gaskett Analytical Services

Nash House, Robbets Industrial Estate, Mail Rd
Orpington, Kent, BR5 5PH

Telephone 021212 614892
email pork@gaskett.truenet.uk

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This new company in the analytical field has made a serious impact on the market within a short time. Our newly acquired range of instrumentation guarantees turn around times for samples within 48 hours. Our labs are set up to perform the most exacting analysis using techniques such as:

- UV analysis
- Infrared
- GC-FID
- HPLC with diode array detection
- Capillary electrophoresis
- ICP-MS

We boast a growing staff of 12 personnel, many of whom have had recent links with institutions recognised as leaders in the analytical sciences. It is our aim to build a state-of-the-art laboratory capable of carrying out the most exacting analytical tasks to the highest quality.

For further information Contact:

Peter Pork

Peter Pork on 015324 797395

Proprietors P. Pork HND & U.R.A. Gaskett

Aqueous samples costing guide

(Note this is intended for illustrative purposes only. For detailed quotation please apply)

Analysis Type	No of samples	Cost per sample £
UV analysis	1-10	10.00
	10-50	8.00
	> 50	5.00
Infra red		
Solid samples	Per sample	15.00
Liquid samples	Per sample	15.00
Air samples	Per sample	200.00
GC-FID		
Aqueous samples with liquid-liquid extraction	Per sample	35.00
Aqueous samples - no extraction	Per sample	15.00
Solid sample with Soxhlet extraction	Per sample	22.00
HPLC with diode array detection		
Aqueous samples with liquid-liquid extraction	1-10	35.00
	10-50	22.00
	> 50	15.00
Aqueous samples - no extraction	1-10	15.00
	10-50	10.00
	> 50	8.00
Solid sample with Sohxlet extraction	1-10	22.00
	10-50	15.00
	> 50	12.00
Capillary electrophoresis	Contact us for a detailed quote	
ICP-MS		
Organo tin solid	Per sample	40.00
Organo tin Aqueous	Per sample	25.00

All prices exclude VAT

	diquat dibromide	**p-octylphenol**	
	aqueous µg /l	aqueous µg /l	sediment ppb
LOD	0.05	0.1	1.4
Turnaround time in hours	24 hours	48 hours	

STS Labs Ltd

Your BEST choice for speedy and reliable outsourcing

STS Labs Ltd (established in 1974) was one of the first ISO 17025 accredited laboratories in the country. Our expertise is in environmental analysis and we believe that effective environmental management is a cornerstone of successful business. STS is a leading provider of environmental testing services and consultancy.

STS serves a diverse range of markets that depend on analytical science including food & agriculture, life-sciences, forensic and environmental sectors. In addition to the provision of analytical services STS has considerable experience in the validation and development of analytical methods. We offer UKAS accredited methods of analysis.

We are leading specialist in all aspects of ICP spectroscopy as well as offering HPLC, GC, GC-MS, electrophoresis, AAS, and FT-IR facilities.

Our comprehensive environmental monitoring service is unrivalled in Europe. Simply inform us of your requirements and we will design a complete program to address your monitoring requirement right through from sampling to data analysis.

STS only employ highly competent and experienced chemists who, combined with modern instrumentation, provide the means of meeting the increasing demand from industry, local authorities and the environment agency for fast accurate analysis.

Assaying operations are centred at STS's Main Laboratory in Skegness.

STS

	diquat dibromide	**p-octylphenol**	
	aqueous µg /l	aqueous µg /l	sediment ppb
LOD	0.05	0.5	1.0
Turnaround time in hours	96 hours	192 hours	

STS Labs Ltd. Analysis request form.

Enter the required information for an instant email quotation

Name				
Address				
Telephone/ Fax				
email				
Compound(s)	Matrix	No of samples	Detection limit required	Required turnaround time

Ask for details of our ongoing analysis all inclusive service

STS Labs Ltd. Analysis request form.

Name	
Address	
Telephone / Fax	
email	

Compound	Matrix	No of samples	Detection limit	Turnaround time	Cost per sample (£)
Diquat dibromide					
Octylphenol					
Octylphenol					

STS Labs Ltd. Analysis request form.

Name	
Address	
Telephone / Fax	
email	

Compound	Matrix	No of samples	Detection limit	Turnaround time	Cost per sample (£)
Diquat dibromide					
Octylphenol					
Octylphenol					

Strudenfarter Analytisher Dienst

About Strudenfarter Analytisher Dienst

We are one of the leading analytical labs specialising in environmental monitoring. Our ultra modern lab is located in a central European position enabling Europe-wide analysis by state of the art automated analytical equipment.

We have a long history of involvement with assessment of water quality including:

- pond and lake water quality
- causes of fish mortality
- pollution of rivers and streams
- sea water quality at beaches
- ground water contamination by organic or inorganic contaminants
- pollution of marine and estuarine environments by mineral oils
- surface water classification **(75/440/EEC)**
- suitability for irrigation
- presence of UK "Red List" contaminants
- suitability for aqua-culture, horticulture and general amenity uses

Sediment samples are also taken and analysed as part of the firm's work with ponds and lakes. Advice is also given on treatment and on the possibilities for use in landscaping or safe disposal off-site.

People in the Western World, making use of the numerous appliances in their homes, often are taking for granted access to large quantities of the clean water - consistent in composition and free from harmful bacteria. Apart from drinking needs, water may be required for washing, cleaning, watering the garden and filling swimming pools. Although water companies supply good quality drinking water, problems can arise within complex or modified distribution systems, particularly in large buildings.

Waters for human use are analysed by Strudenfarter Analytisher Dienst on a regular basis and advice is given on suitability, e.g.:

- Waters for Potability **(80/778/EEC)**
- Natural Mineral Waters **(80/777/EEC)**
- Bathing Waters **(76/160/EEC)**
- Purified and Injection Water (BP)
- Well and Borehole Waters

Aqueous samples

	Euros
Ammonia	5.00
Free cyanide	20.00
Total cyanide	21.00
Detergents (ionic)	28.00
Detergents (non-ionic)	110.00
Organo tin ICP-MS Aqueous Sample	75.00
Orthophosphate	5.50
Phenol (Total monohydric)	12.50
Phenol (speciated)	82.50
TOC	12.50
Metal screen ICP-MS	42.00
TON	4.50
GC-MS Semiquant scan	205.00
Glycols	8.00
Organo phosphate pesticides	135.50
Organo chlorine pesticides	110.00
Bipyridylium pesticides	80.00
Alkylphenols	78.00
Poly Aromatic Hydrocarbons	100.00

Solid samples

Poly Aromatic Hydrocarbons	82.00
Poly Aromatic Hydrocarbons screen(GC-FID)	36.00
Volatile Organic Carbon	82.50
Organo phosphate pesticides	140.00
Organo chlorine pesticides	110.00
Synthetic pyrethroids (GC)	110.00
Organo tin ICP-MS Solid Sample	82.00
Alkyl phenols	85.00
Total petroleum hydrocarbons	98.00
Oil ID	90.00

	diquat dibromide	**p-octylphenol**	
	aqueous µg /l	aqueous µg /l	sediment ppb
LOD	0.1	0.5	0.5
Turnaround time in hours	96 hours	96 hours	

All costs are inclusive of transport charges
All techniques are NAMAS accredited.

Strudenfarter Analytisher Dienst
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Wartanal provides through our Analytical Service group, a comprehensive range of testing and analysis facilities. Investment in modern instrumental techniques enables the business to handle enquiries related to; occupational hygiene, contaminated land, groundwaters and wastewaters, forensic sciences, metallurgy and condition monitoring.

Determinations from trace to macro levels in a wide variety of matrices, e.g. pesticide residues, product development, storage stability, clinical trials. All our techniques are UKAS accredited. We also contribute to a number of UK and International proficiency testing schemes and are ISO 17025 accredited.

The principal activities of the analytical facility are provided from the following range of techniques:-

- **Spectroscopy** ICP-OES, XRF, OES, FT-IR, AA
- **Chromatography** GCMS, HPLC, IC, GC-ECD, GC-FID
- **Electron microscopy** optical microscopy, x-ray diffraction
- **Thermal analysis** TGA, DTA, DMA, DSC

If your requirements are not listed above please phone. The laboratory will provide data reports or a comprehensive interpretation as required.

Wartanal *analysis suite*

Toxicity Testing			Cost £ /sample
Ecotox	5 min	15 min	60.00
Daphnia	24 hr	48 hr	600.00

Metals	Cost £ /sample		Cost £ /sample
Ag	6.00	Hg	9.00
Al	6.00	Mg	6.00
As	6.00	Ni	6.00
Cd	6.00	P	18.00
Cr	6.00	Pb	6.00
Cr(VI)	16.00	Sb	12.00
Cu	6.00	Se	15.00
F	6.00	Zn	6.00
Fe	6.00	Metal screen ICP-MS	30.00

Oxygen demand	Cost £ /sample
BOD	15.00
COD	16.00

Miscellaneous Analysis	Cost £ /sample
Ammonia	3.20
Free cyanide	14.50
Total cyanide	14.50
Detergents	
Ionic	20.00
Non-ionic	80.00
Dissolved oxygen	4.00
pH	4.00
Organo tin ICP-MS Aqueous Sample	40.00
Organo tin ICP-MS Solid Sample	55.00
Orthophosphate	4.00
Phenol (Total monohydric)	9.00
Phenol (speciated)	60.00
TOC	9.00
TON	3.20
GC-MS Semiquant scan	150.00
Glycols	60.00
Total petroleum hydrocarbons	60.00
Oil ID	65.00
Surfactants Solid Sample	75.00
Surfactants Aqueous Sample	60.00
Organo phosphate pesticides	100.00
Organo chlorine pesticides	80.00
Bipyridylium pesticides	60.00
PAH (EPA-16 protocol)	60.00
VOC suit	60.00
PAH screen (GC-FID)	26.00
Synthetic pyrethroids (GC)	80.00

Prices quoted are based on a seven day turnaround and a minimum of 10 samples per analysis. For sample numbers of less than ten, a 20%premium is charged. A 25% rebate is available for a cumulative total of 100 samples or more over a 12 month period. For 24 hr service add 25% to the cost.

	diquat dibromide	**p-octylphenol**	
	aqueous µg /l	aqueous µg /l	sediment ppb
LOD	0.5	5.0	1.0
Turnaround time in hours	36 hours	36 hours	

Please enquire about further discount rates which maybe available on bulk samples. Further information is available from:

Wartanal, Unit 34, Crosby Science Park, Pearl Drive, Nottingham, NG4 7HQ
Tel 01932 7777777 Fax 01932 7727777
Email Wart@anal.compuspu.co.uk

STS **Labs Ltd.** Analysis request form.

The quotation is as follows: -

Name	
Address	
Telephone / Fax	
email	

Compound	**Matrix**	**No of samples**	**Detection limit**	**Turnaround time**	**Cost per sample (£)**
Diquat dibromide					
Octylphenol					
Octylphenol					

All costs are exclusive of VAT
Note; We can arrange sample collection on the above samples at the following cost:
£200 + VAT per excursion

STS **Labs Ltd.** Analysis request form.

The quotation is as follows: -

Name	
Address	
Telephone / Fax	
email	

Compound	**Matrix**	**No of samples**	**Detection limit**	**Turnaround time**	**Cost per sample (£)**
Diquat dibromide	Aqueous	720	$0.1\ \mu g\ l^{-1}$	7 days	51
Octylphenol	Aqueous	900	$1.0\ \mu g\ l^{-1}$	28 days	47
Octylphenol	Sediment	675	$1.4\ pg\ g^{-1}$	28 days	54

All costs are exclusive of VAT
Note; We can arrange sample collection on the above samples at the following cost:
£200 + VAT per excursion

Author	Tina Overton, Simon Belt, Stephen Summerfield
Title	A Dip in the Dribble Problem-Based Learning Case Study
Classification	Case Study
Keywords	sfsoer, ukoer, chemistry, environmental, analytical, case study, problem-based learning
Description	Appendix A
Creative Commons Licence (url)	http://creativecommons.org/licenses/by-nc-nd/2.0/uk/
Language	English
File size	600 kB
File format	pdf