UNIVERSITY OF HULL

Titan Project 2009

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Appendix A: Student Handouts

The Titan Project

Titan Industries, a major manufacturer of titanium dioxide with developing interests in the Asia Pacific region, has just purchased a 10-year-old titanium dioxide plant in Kerala, on the south-east coast of India. The plant manufactures anatase by the sulphate process.

As the management team, your mission is to recommend a five-year plan for the site.

Your options include

- continuing to operate the plant as is
- replacing it with a larger sulphate process plant
- replacing it with a chloride process plant
- licensing new technology inTiO_2 manufacture
- expanding into new markets

Any imminent expenditure plans need to be fully justified.

Consider

- The state of the TiO_2 industry in India and the Asia-Pacific market.
- Details of the sulphate (SP) and chloride (CP) processes
- Recent performance of the purchased plant
- The advantages / disadvantages of SP and CP
- New technology for TiO_2 production
- What the various options are for the site are
- Whether the infrastructure, demographics, educational standards, public health standards and environmental standards are appropriate for any new installation.

The Titan Project

SCIENTIFIC SKILLS

- industrial chemistry
- the pigment industry
- environmental & safety issues
- economics
- political and social context
- analytical methods
- statistics

TRANSFERABLE SKILLS

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

The Pigment Industry

You are the existing management team empowered by Titan Industries (TI) to make recommendations on the future of a newly acquired plant in India. The plant uses the sulphate process to produce anatase. TI is expanding into the Asia-Pacific market, and wants to explore adding specialty grade TiO_2 to its product range. The following report has been prepared and is considered highly relevant to your project.

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TiO_2 is the most widely used white pigment in the world. Coatings, paints plastics, ceramics, inks, and fibres all depend on white pigments to impart colour and opacity.The market has an annual valuation of over $9 billion.

Producers and analysts estimate global growth for TiO_2 at around 2-3%/year. Asia is the fastest growing market with projections of future growth rates of 6-7%/year. However, there is concern that TiO_2 capacity is being added globally at a quicker rate than demand is growing.

Titan Industries (TI) is one of the top 5 titanium dioxide producers in the world. TI has just bought the TiO_2 businesses of Titanium Productsof India, an Indian producer, in a multi-billion pound deal. The acquisition included a plant in Kerala, on the South West coast of India, and is part of an ongoing long-term strategy to expand into the Asia-Pacific market. The Kerala facility has specialised on production of anatase by the sulphate process.

The aim of the company is to rationalise operations and efficiency at specific sites and to capture a larger market share, especially in specialty grades of TiO_2 when demand increases. This includes the possibility of expansion into the rapidly developing high-tech applications of TiO_2 This will be financed by the sale of non-core subsidiary companies over the next few years. However, at this time the company has a cash flow problem.

Raw Materials

The titanium dioxide industry uses the following minerals as the initial raw material - the average content of TiO_2 is given in brackets; **ilmenite** (35-65%), **rutile** (90-98%), **synthetic rutile** (85-96%), **titanium slag** (70-85%).

The Sulfate Process (or 'wet process'):

The older method of industrial TiO_2 production and requires either the cheaper ilmenite ($FeTiO_3$) or titanium slag as a starting material. Key steps in the process are:

1. **Benefication** (Pre-treatment)**:** This involves milling, screening and drying of raw materials followed by removal of any metallic iron using magnets.

2. **Acid Digestion:** The prepared ore is then digested in sulfuric acid. This process takes around 12 hours and involves the addition of concentrated sulfuric acid to the ore in the presence of water. The result is a solution containing titanium and iron species.

   $$FeTiO_3 + 2\,H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + 2\,H_2O$$

3. **Washing:** The 'cake' produced by the acid digestion is then washed with warm water (or dilute acid) to remove as much iron sulfate as possible.

4. **Hydrolysis:** Hydrolysis of the resulting Ti species gives a hydrated form of titanium dioxide and free sulfuric acid:

   $$TiSO_4 + (n+1)\,H_2O \rightarrow TiO_2.nH_2O + H_2SO_4$$

   The hydrolysed gel must be removed and washed quickly to prevent dissolution in the liberated sulfuric acid. Seeds of the required TiO_2 product crystal structure are added..

5. **Washing, Doping:** After washing to remove the majority of the sulfuric acid, small amounts of any required additives are added.

6. **Calcination:** The hydrated gel is heated in rotary kilns in the presence of excess air. Careful temperature control is essential.
   - For anatase production, a final temperature of 800 - 850^{o}C is necessary (the hydrated gel having been seeded with anatase crystals).
   - For rutile production a higher final temperature of 900 - 930^{o}C is required (the hydrated gel having been seeded with rutile crystals).

7. **Milling:** once cool, the titanium dioxide produced can be milled and surface treated in order to obtain the desired refractive properties from the pigment.

The Chloride Process (or 'dry process')

This process was developed in 1957 as an alternative large-scale route to titanium dioxide and requires rutile (preferably with a TiO_2 content of around 95%) as a starting material. Key steps in the process are:

1. **Pre-treatment of the ore:** The crude ore is finely ground and thoroughly dried.
2. **Formation of $TiCl_4$:** The rutile is heated to 800 to 1200^oC in a stream of chlorine gas and in the presence of coke.

$$TiO_2 + 2\,Cl_2 + C \rightarrow TiCl_4 + CO_2$$

3. **Reaction with oxygen:** The pure titanium tetrachloride is pre-heated and reacted with oxygen at 900 - 1400^oC to give TiO_2. The chlorine produced can be recycled.

$$TiCl_4 + O_2 \rightarrow TiO_2 + 2\,Cl_2$$

The product produced is rutile. The quality of the product is affected by factors such as temperature, stoichiometry of reaction with oxygen, method of mixing.

4. **Milling:** The product is ground to the particle size required by the end user of the pigment and, where necessary, treated with surface agents.

A New Process from Altair. (Press releas)

The Altair TiO_2 pigment processs (based on the first comprehensive patent for a TiO_2 production since DuPont's chloride process 50 years ago) is based on hydrochloric acid leaching of the low grade ore ilmenite at high-acid concentration. This is the same raw material as used in the sulphate process. Titanium is transferred by solvent extraction into a high-purity aqueous stream with a high titanium concentration. HCl gas is recovered by pressure-swing distillation and is used to regenerate the leaching solution. The Altair process recycles all chloride waste streams. A new method of TiO_2 recovery in dense film with simultaneous dehydration and hydrolysis provides great flexibility in adjusting the characteristics of the TiO_2 pigment product. The process is capable of producing either anatase or rutile by control of process variables. Modifications of this method lead to a flexible, low-cost, high-tonnage process first for the production of nano-sized TiO_2.

Sulfate vs. Chloride Process

Since its introduction in 1950's, the *Chloride Process* (CP) has steadily grown in importance. In the early 1990's, CP overtook the *Sulfate Process* (SP) as the dominant source of commercial TiO_2. In the 1980's the proportion of Sulfate Process produced TiO_2 was about 65% and today has fallen to 35%. This trend is expected to continue. The last sulphate plant in the US closed in 2004.

- The CP is a continuous process whereas the SP is a batch process.
- The SP can produce both rutile and anatase forms of TiO_2, whilst the CP is limited to rutile production. This can be a major benefit as no contamination of high quality rutile with anatase occurs. Rutile has been shown to be an acceptable substitute for anatase in food applications.
- The waste produced during the SP is the main problem with this method and can amount to 3-4 tonnes of iron sulfates and 8 tonnes of dilute acid per tonne of TiO_2 produced. However, solid waste can be useful and saleable Iron salts sold to the water supply industry for use in the manufacture of water purifying products. Also used extensively as soil additives. Gypsum is sold as $_s$oil fertilisers for farming and used in the manufacture of building materials such as plasterboard etc. Sulfuric acid can $_b$e reclaimed and $_t$he remains recycled.
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- The CP is seen by many as the least environmentally damaging and was developed partly because of the huge amounts of waste produced during the SP. However some problems are presented, including the controlled handling of large amounts of $TICl_4$ and use of potentially hazardous Cl_2. The process was introduced at a time when CO_2 was not considered a pollutant. CO_2 is produced by the chloride process in the carbothermal rection of the ore with carbon and chlorine at a rate of 44 tonnes of CO_2 per 80 tonnes of product TiO_2.
- Low capital investment is required to set up a SP plant and begin production. CP plants are considerably more expensive to set up. Running costs are also significantly higher for the CP, due to power demand (and thus greater CO_2 production), and also the higher cost and lower availability of the raw materials, although overall efficiency is higher due to the huge production capabilities of a modern CP plant.
- The CP *must* be used for preparation of TiO_2 with a final destination in vehicle top coats and PVC. These uses represent about 10% of the world titanium dioxide demand. On the other hand, the SP *must* be used for production of high performance anatase, used in high quality paper and ceramics.

The Altair Process (AP)

- AP is similar in some sense to CP but uses ilmenite as a starting material
- AP is a batch process.
- AP can produce either anatase, rutile or nanoparticulate TiO_2.
- Iron salts are by-products in AP.
- No acid waste is produced, and no CO_2.

Altair will construct any new AP plant to users specification.

Questions

Pigments
(You will find the *Kirk Othmer Encyclopaedia of Chemical Technology* or something similar useful as a starting reference.)

1. Discuss briefly the characteristics desirable in a good pigment.

2. Make a short list stating the specific advantages and disadvantages of both rutile and anatase pigments as a consequence of their distinct properties, explaining briefly how these different properties affect their end uses.

3. If rutile appears slightly yellow in colour, what region of visible light does it absorb? Why is the absorption of UV radiation a problem in the use of TiO_2 pigments?

4. What are some applications for nanoscale TiO_2?

The Titanium Dioxide Industry

5. What is meant by a 'green field development'?

6. The two established industrial methods of preparing titanium dioxide are the *Sulfate Process* and the *Chloride Process.* For **each** of these processes give a list (with brief explanations) of its advantages and disadvantages and compare each with the Altair process..

7. Iron chloride is a by-product of the Altair and chloride processes. What are its industrial uses?

8. List some reasons why it is not usually desirable to run an industry at full capacity (100% production rate) for extended periods.

The Future of the Kerala Site

Your mission is to assess the newly acquired Kerala site, weigh up the possible options and recommend the best plan for the future. Due to the current financial situation, any imminent expenditure plans must be well argued and fully justified. It is the aim of Titan Industries to be the maintain its number one pre-eminence as a global producer of titanium dioxide, maximise profits and utilise capacity to the full.

The map shows the location of the site in Kochi, Kerala. It is TI's only operation in India. The company are looking for a way of breaking into the Asia Pacific market, especially for high purity TiO_2. Until now TI has been involved almost exclusively in Chloride Process production plants (regarding the Sulfate Process as yesterday's technology), but this site contains one of several Sulfate Process plants in India.

The State of Kerala

Kerala lies between the Arabian Sea and the Western Ghats mountain range in southwest India (see map). The mountain region now produces hydroelectric power. It is an area of natural beauty and has a significant tourist industry as well as a developed chemical industry. The two are uneasy partners in the regions prosperity. The state has enjoyed double the national rate of business growth since 2000.
The state population of 32 million has among the highest literacy, educational and health care standards in India. Kerala was top of the national Educational Development Index for 2006-7.
Industrial relations have had a difficult past, but great improvements have been made.

The Town

Kochi is the second largest city in the state of Kerala, and is one of the most important seaports in India. Once a relatively stagnant local economy, it has enjoyed spectacular development since 2003, and is a centre for tourism, IT and international trade. It is the commercial hub of Kerala. Various technology and industrial campuses operate in the outskirts of the city, The Kochi International Airport is also expanding.

Eloor, situated 17 km north of the Kochi and is the largest industrial belt in Kerala, with more than 250 industries manufacturing a range of products including chemical and petrochemical products, paints, pesticides,paper, ceramics, rubber processing chemicals, foodstuffs and leather products.

The Site

The site consists of a large area of land in Eloor, near Kochi. It includes a dock facility, and plenty of room for future development and building (only a quarter of the land has been developed). It is well connected by road and rail. The operational Sulfate Process plant is currently profitable but has had a mixed recent history. It is old and requires refurbishment and updating to conform new environmental legislation.

The majority of the waste products from the sulphate plant, including sulphuric acid, are currently being pumped out into the coastal waters via a short pipeline, with some of the solid waste going to landfill. The position of the site allows easy import/export of bulk materials to the Asia Pacific market.

The Market

Analysts predict a steady upswing in the TiO_2 industry over the next 15 years, particularly in the Asia - Pacific region where your company is trying to establish itself as a dominant force. Experts predict increased competition in the European sector. Careful planning is essential, as all companies will be looking for ways of increasing output over the next decade to stake a claim on the predicted demand increases.

Local Industry

There are numerous interactions with local industries in the Eloor Industrial Belt, which, in addition to the wider issues, that could have a bearing on your decisions.

Nature Reserves and Tourism

Nature tourism is a recent development in Kerala and contributes significantly to the economy of the state. Tropical fauna, in particular birds, are protected in several sites in the inland National Parks, and at sites along the Arabian sea coast. Sport fishing has also developed after the decline of the local fishing industry due to the appearance of Japanese factory ships which have depleted commercial fishing stocks. Four resort hotels have been built in the area, including two on the coast. Many new businesses have also appeared throughout the town to cater for the increasing number of visitors New hotels are under construction along the coast

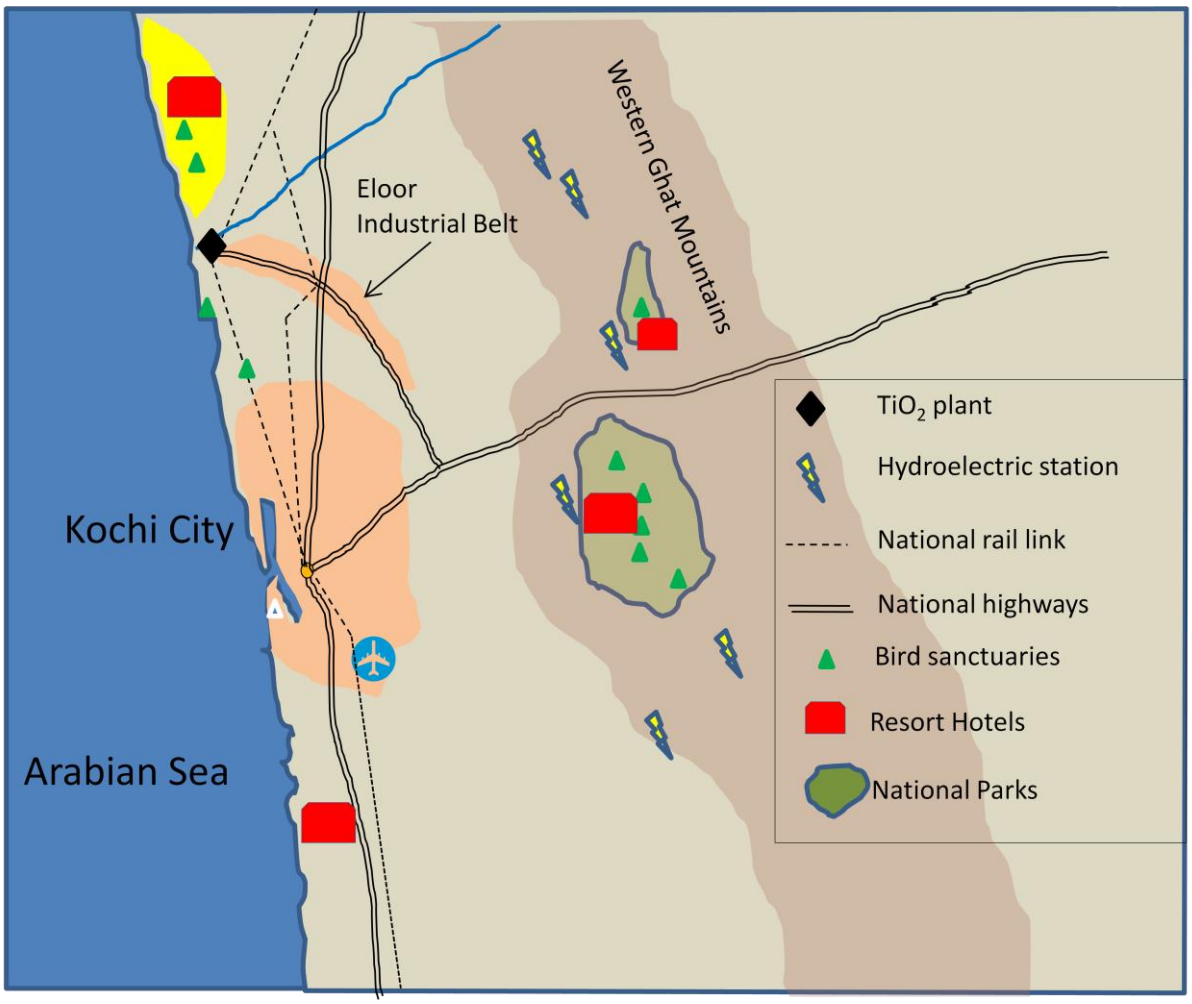
Your Mission

- **List reasons why the site is a good location for a TiO_2 plant in the context of TI's global interests..**

- **Propose a strategy for the next 5 years of TiO_2 production at the site.**
  You have to recommend either the development (with acid recycling and other waste disposal remediation) or closure of the current sulfate process plant and whether or not to construct a more expensive chloride plant at the site. You should also consider the option of a new facility for high purity TiO_2 using technology licensed from Altair using ilmenite, possibly by a joint venture with Altair (Now called Altairnano) Remember there will be a big political and public pressure on TI so the **environmental, employment** and **public safety** issues need to be considered for whatever option you recommend**.**

- **Presentation of Recommendations**
  Your spokesperson must present your proposals for the next 5 years to a panel of higher managers (2 or 3 tutors) justifying all your decisions. It is important that you state the group decisions in a coherent and persuasive manner.

Map of Kochi (State of Kerala)



Recent Articles from the Trade Press

General Market figures.

Producers and analysts estimate global growth for TiO_2 at around 2-3%/year. Asia is the fastest growing market with projections of future growth rates of 6-7%/year.

The market outlook for titanium minerals, ilmenite and rutile, is positive, buoyed by strong growth in all end use sectors.

Ilmenite production is distributed in the following way: Australia - 46%, Norway - 13%, Ukraine - 12%, USA - 8%, India - 8%, China - 4%, ROW - 9%.

The Balla Balla ore deposit in Western Australia contains over 500,M tonnes of ilmenite. The The Balla Balla ore deposit, in Western Australia contains ~600 million tonnes of ilmenite ore, and is scheduled to be mined in mid-2009, to produce in excess of 480,000t per annum of ilmenite.

Competitor Performance

Titanium Productas of India
For the financial year to end-March 2003, Titanium Products of India Ltd (TPI) reported a small net loss for the first time since it began operating in the early 1950s due to prices for anatase TiO_2 pigments in the Indian market, which in turn has been due to alleged dumping of anatase TiO_2 from Chinese suppliers.

To create new profitable opportunities, TPI has decided to embark on making rutile TiO_2 pigment grades, whereas it has hitherto manufactured only anatase.

TPI is spending Rup 160-200 M to install a **captive hydroelectric power generation.** Mr I.V. Invallam (Managing Director) stated that these new facilities will help the company to reduce unit manufacturing costs and cater for increased requirements in line with the pigment expansion programme. However TPI is "still considering" a Rup 1.1 bn investment to substantially reduce environmental damage arising from waste effluents. The company plans to raise its capacity to 33,000 tonnes/y at a cost of $55 M. (See also 'Focus on Pigments', Nov 2006, 5). Sulfuricacid requirements are met from a captive on-site brimstone-based sulfuric acid plant.

Recent Environmental Issues at TPI Sulfate Anatase Plant in Kerala.Titanium Products of India(TPI) has been ordered by the Supreme Court Monitoring Committee on Hazardous Wastes to speed up work on the implementation of pollution control measures at its Eloor sulphate TiO_2 plant.The plant has always discharged virtually all its spent acid and iron waste into coastal waters.. Local residents and fishermen have protested about this for many years and at times they have blocked the effluent pipeline, forcing TPI to temporarily suspend pigment production.

In May 1995, the Kerala Ministry of Health served a "notice of closure" on the TPI plant. But, a "stay of execution" was granted when the company promised to improve pollution control measures. Ten years later, the Kerala Government approved TPI's plans to double pigment capacity to 30,000 tonnes/y at the same time as installing a waste acid recycling unit and establishing a dedicated on-land site for dumping solid wastes. The deadline for installing the acid recycling unit was 26 April 2006. Just three months away from the deadline, TPI had not even awarded an engineering contract for the project.

Kerala as a Destination for New Industries
(summaries from various sources)

Health Care.
India's maternal mortality rate (MMR) stands at 450 per 100,000 live births -- against 540 in the 1998-99 period -- and way behind the Millennium Development Goals (MDGs) which call for a reduction to 109 by 2015, the United Nations Children's Fund (UNICEF) said.
While the northern state of Uttar Pradesh has a maternal mortality rate of 517, almost comparable to Sudan at 550, the MMR in the southern state of Kerala is only 110.
(Reuters, Jan 2009)

Labour Relations

From Venture Management Associates.
Over the last few years, there have been absolutely no issues of problems raised by organized labour. As a result, there isa change in the investment climate and after the recession, Kerala should see investors making it a destination,Elamaram Kareem, Kerala industry minister, also notes a new maturity in the trade unions.

This change in attitude has encouraged the government to start discussions with private firms in sectors such as information technology, biotechnology, tourism and chemicals for investments in the state, he says.

(adapted from Wall Street Journal, Jan 2009)

3. Infrastructure

New Delhi, Jan 15 The central government Thursday approved the Rs.13.3-billion road expansion schemes for National Highway 47 in Kerala.

(Sindh Today, Jan 2009)

4. Education and workforce resourc
Kerala's education systemis one of the most literate states in the country. English is the language of instruction in most private schools;government run schools offer English or Malayalam as medium. After 10 years of secondary schooling, students typically enroll at Higher Secondary School in one of the three streams—liberal arts, commerce or scienceStudents can then enroll in general or professional degree programmes. Kerala topped the Education Development Index (EDI) among 21 major states in India in year 2006-2007**Rutile Market Prospects**

Rutile TiO_2 just as acceptable as anatase TiO_2 for food colouring
TiO_2 –based pigments have been used as food colorants for many years. Icecream, peppermints, chocolate coated mints and certain types of cheese (eg *Mozarella*) often contain TiO_2. Traditionally, European and US regulations stipulated that only anatase could be approved as food colorants.
A joint working party established by the Food & Agricultural Organisation (FAO) and the World Health Organisation (WHO) has concluded that the bioavailability of rutile grade TiO_2 pigment is y the same as that of anatase. Based on this finding, the European Food Safety Authority has ruled that rutile grades and anatase grades will be equally permissible as food colorants.

(Food Chemical News, 12 Sep 2005, 47 (31), 18)

New Markets for high grade TiO_2

The Japanese Experience

Virtually all the Japanese TiO_2 producers have been keen to diversify into producing speciality grades, including nanoparticulate grades used for multilayer ceramic chip capacitors (MLCCs), photocatalysts, denitrification catalysts and ultraviolet shielding agents. The photocatalytic properties of TiO_2 are being used for new applications including deodorisers, antifogging agents, antifoulants, antibacterials and air purification. **The domestic market in these areas amounts to only about 140 tonnes/y at the present time, but this is worth an estimated Yen 30 bn. In 2002, Japan's demand for purified grades of TiO_2 for use in MLCCs amounted to 2600 tonnes, while demand for general purpose grades was 2000 tonnes.** *(Japan Chemical Week, Sept 2004)*

Demand for photocatalytic TiO_2 is also increasing, especially for various environmental applications. In Japan, these applications include: filters in air cleaners and air conditioning systems; road paving materials; traffic paints; worktops and ceramic tiles; exterior construction materials and tents. The Photocatalysis Industry Association of Japan estimates total sales revenues of member companies of Yen 27.3 bn in 2004, *(Japan Chemical Week, 19 Oct 2006, 47 (2388), 4–5)*

Tayca Corp is budgeting Yen 2 bn for the construction of a new unit at its Okayama complex, which will be capable of producing 1200 tonnes/y of nanoparticulate TiO_2 and zinc oxide. The unit should be ready for start-up in 2Q 2009. It will be sited alongside a 1400 tonnes/y unit, which came on-stream in 2005. For 2010, Tayca is forecasting annual sales revenue of Yen 3 bn from nanoparticulate grades.

*Japan Chemical Week, 14 Feb 2008, 49 (2453), 2**US***

Prospects US demand for TiO_2 for use in denitrification catalysts rose to 20,000 tonnes in 2003, as a result of tighter controls on the emission of nitrogen oxides from thermal power plants. However, subsequent postponement of the regulations by the environmentally hostile Bush Administration led to a sharp fall in demand The election of the more environmentally aware Barak Obamahas revived the prospect of a huge growth in denitrification catalysts, based on TiO_2 . A parallel increase in waste-water cleanupusing TiO_2-based photocatalysis is anticipated. Iron chlorides, valuable by-products also have a well developed market in waste water treatment. The environmental outlook for high grade TiO_2 is promising.

(Chemistry and Engineering News, Dec 2008)

Press Release from Altair and Goodman Engineering.

Altair and Goodman Engineering today announced details of their recently formed joint venture, "Altairnano Goodman Titania, Inc." (ATI, which brings together Altair's TiO_2 manufacturing process with Goodman's engineering expertise to develop, design, construct and commission manufacturing plants to produce , especially in emerging countries that increasingly use titanium dioxide based pigments in paints for housing, automobiles and in plastics. These countries have had, and continue to forecast, high growth rates (e.g. 15%) for pigment consumption.

TiO_2 The project uses the Altair Hydrochloride Pigment ("AHP") process to extract titanium and to manufacture titanium dioxide pigment from low cost ilmenite.,. ATI The AHP Process is a disruptive technology because it threatens the TiO_2 pigment supply chain established over the last 50 years. It enables companies in emerging markets such as China, India, Southeast Asia and Africa to enter the TiO_2 pigment supply market with an environmentally friendly manufacturing process that has a cost structure substantially lower than current supply methods. The Altair Process is economic for plants producing 30,000 tons a year to large scale manufacturing exceeding 100,000 tons per year. This is an important capability in emerging economies and to specialist pigment producers as it enables these smaller companies with limited capital resources to affordably enter the market. These plants can be readily expanded to larger

scale manufacturing operations as customer demands grow.

Kerala Chronicle

Bringing Keralites the World

Volume 17 Issue 25 **Serving Kerala.**

Legislative Assembly Elections Loom

Local Assembly Member for Kochi East, P.T. Valsamma officially opened his election campaign on Tuesday to a packed hall. As he put it 'the two biggest issues facing Kochi, and Kerala too,' are unemployment and the environment. A representative of the local tourist board said later that he was encouraged but remained yet to be convinced.

'Industry must clean up act'

After a lengthy investigation, the Kerala Water Authority has condemned local industry for its poor pollution record.

A report issued this week highlights the need to clean up the Kerala Backwaters and the rivers Periyar and Pamba. Local environmental groups (supported by Local Assembly Member P.T. Valsamma) have called for a dramatic reduction in waste discharged into the waterways of Kerala over the next 3 years.

A further investigation is to follow and all industries have been asked to provide an environmental statement on their present and future plans to clean up the river.

A team of experts is currently investigating the effects of pollution on local wildlife at the Peryar National Park

Residents Fear Poison Gas

Local residents of North Kochi have formed a protest group. They are concerned to read about a recent accident at an American chemical plant owned by Titan Industries, who have recently acquired the Eloor titanium dioxide manufacturing site. System failure at the US plant was blamed for the uncontrolled release of chlorine from a titanium dioxide plant.

Mrs K. Yohannan (78) spoke for the concerned residents, "This could happen here.". Reports of the accident were posted through many doors in the area by an unknown pressure group.

Workers Save Mill

Two months ago, the Eloor Paper (EP) Ltd. paper mill, North of Kochit faced almost certain closure. Today, however, managers are discussing expansion plans after securing a new contract with the state government. EP Ltd. will supply high quality heavyweight 'whiter than white'paper for use in official documents in a 10 year deal of undisclosed value.

A spokesman Suresh Beenamol said 'The credit must go to our workers. The industrial disputes which plagued our company are a thing of the past' EP is hoping to employ 100 more staff

Refuge For Nature

Our second success story this month involves the renovation of a large piece of land to the north of the town. The windswept marshes and sand dunes of Ranji Beach would still be a polluted wasteland if it hadn't been for the discovery of local fireman

Ranesh Kanoor (32) told The Chronicle 'I was walking along the beach when I saw a funny looking bird. I didn't think much of it, but told my wife, Mrs Kanoor'. Mts Kanoor (29) later went back with a book and told us, 'The bird, which was tired and lethargic, turned out to be a Norwegian Blue a rare breed of parrot long thought to have died out on the Subcontinent, and soon the place was full of ornithologists'.

The nature reserve was opened 14 months ago and has seen thousands of visitors including a regular stream of school 'field trips'. The purpose built visitor centre and hotel will soon be extended to provide another restaurant and a huge interactive nature exhibition. There is also talk of building a 'sea life' centre and a small theme park to the south of the reserve. The reserve is home to many rare species including red squirrels.

Political Row over Water Treatment Plant

At a recent dinner, local Assembly Member P.T Valsamma claimed credit for the soon-to-be-opened water treatment plant as part of his 'Environment and Employment' campaign. However the opposition claim that the Kochi East Assembly Member has had little to do with the development until recently and in fact that the plant was well behind schedule, and had been mandated by the courts 10 years ago.

The plant should have been operational this year, and should have a major effect on the state coastal waters.

Titan to Send in Top Management Team

US based Titan Industries is to send in experts to decide on the future of the Eloor titanium dioxide site which it bought recently.

Much ill feeling has surrounded the take-over but as union representatives said yesterday, "We can only wait and see what will happen".

News in Brief

Cheaper Power

Western Ghats Electricity announces cheaper electricity for it's industrial customers in Kerala with the opening of its new hydro-electric plant. The announcement is seen as an

attempt to encourage more industry to the area north of the estuary.

Unemployment Down Again

The fall in unemployment is mainly due to the surprising growth in tourism and related services as a result of the flourishing nature reserve.

The Titan Project

On the basis of your recommendations Titan Industries has decided:

- to dismantle the present Eloor sulphate plant.
- to build a new chloride plant for rutile manufacture.
- to license new HCl based technology from Altair for a smaller plant on the same site for high spec nanoparticulate TiO_2.
- not to defer building a dedicated chloralkali plant for chlorine and HCl manufacture until a large scale Altair Process plant is on-line.

Your task is to recommend a method for the determination of chloride ions in the aqueous effluent.

Survey analytical techniques for chloride

Compare the analytical methods.

Consider the terms accuracy and precision.

Consider what other factors contribute to the choice of an analytical method

Propose and justify your method of choice

Present your recommendation.

The Titan Project

SCIENTIFIC SKILLS

- industrial chemistry
- health and safety
- statistics
- compare analytical techniques
- data analysis / interpretation
- types of error
- accuracy and precision

TRANSFERABLE SKILLS

- working with others
- communication
- decision making
- plotting graphs
- using spreadsheets
- analytical/critical thinking
- time management

What you need to do

Survey analytical techniques for chloride

Compare the analytical methods.

Consider the terms accuracy and precision.

Consider what other factors contribute to the choice of an analytical method

Propose and justify your method of choice

Present your recommendation

Survey of Analytical Methods for Chloride

Following the recommendations that you made to the board, Titan Industries has decided to demolish the current sulfate plant in Eloor, to build a new chloride plant on the site and to enter a joint venture with Altair (to be known as Altairnano-Titan) to manufacture high spec TiO_2 for high value applications A decision on a dedicated chloralkali plant has been deferred.. The new operations require the setting up and refitting of the Process, Quality Control, Environmental Monitoring and Research Laboratories.

You have been directed to investigate the planning and set up of the Environmental Monitoring Laboratory for the new chloride process and the Altairnano-Titan HCl . This is required to meet the stringent environmental legislation and to allay fears of the public to the potential environmental damage from release of chloride ions into the river.

Investigate the methods that could be used to determine chloride ions in the effluent stream.

Consider the following: -

- The advantages and disadvantages of the methods.
- What makes a good method.
- The criteria you would consider when choosing a suitable method.

Present your findings in the form of a short group report.

NOTES

Choosing a Method

1. Give a definition of accuracy?

2. Give a definition of precision?

3. A standard contained 42 mg / l of chloride ions. Five analysts each performed 6 determinations on the same day with the following results.

Analyst A	42.5	41.6	42.9	41.9	41.1	42.2
Analyst B	39.8	43.6	42.1	40.1	43.9	41.9
Analyst C	43.5	42.8	43.6	43.1	42.7	43.3
Analyst D	35.0	43.0	37.1	40.5	36.8	42.2
Analyst E	42.2	41.6	42.0	41.8	42.6	39.0

   Comment on the accuracy and precision for each of the sets of results.

4. How would each of the following influence your confidence in the accuracy and/or precision of the measurement?
   a. Perform the analysis in duplicate.
   b. Perform the analysis in triplicate.
   c. Use an additional method to calibrate your instrument.
   d. Another chemist repeats the measurement using the same procedure
   e. Use two different procedures to obtain the value under consideration.

5. You are required to use an accurately known amount of ethanol (about 5 ml)
   a. Would you do this by volume or weight? Why?
   b. Outline a procedure you would use.
   c. What confidence would you place on the value you obtained?

6. You obtained two values for the purity of an aromatic carboxylic acid. The HPLC method with UV-visible detection gave you 0.5% impurities in the sample and the titration with sodium hydroxide gave it to being 99.8% pure. Can you suggest the reasons for the differences between these figures?

NOTES

A COMPETENT analytical chemist produced the following data based on the methods in *Handbook of Anion Determination* by W.J. Williams

Gravimetric Method

Add 1 ml of 50% nitric acid to 100 ml of water sample. Slowly add with stirring a slight excess of 0.1 M silver nitrate (about 10 ml) The insoluble colloidal silver chloride is formed initially and coagulated upon heating. Test the precipitation by adding a few drops of silver nitrate and allow to stand for 1-2 hours. Filter through a weighed sintered glass crucible, washed with dilute 0.01% nitric acid and dried to constant weight at 110℃ for about 1 hour.

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

Interferences are iodide, bromide, and thiocyanate. Tin and antimony may also cause interferences. Precision is considered better than 0.1%. The following masses were determined four times for each of the chloride standards.

50 mg/l std	100 mg/l std	200 mg/l std	400 mg/l std	800 mg/l std
0.0203	0.0399	0.0805	0.1591	0.3200
0.0200	0.0401	0.0810	0.1596	0.3199
0.0202	0.0398	0.0807	0.1593	0.3202
0.0201	0.0396	0.0808	0.1596	0.3200

Titration: Mohr Method

Add 1 ml of chromate indicator [4.2 g potassium chromate and 0.7 g of potassium dichromate in 100 ml of water] to 100 ml of the water sample. Titrate with a 0.05 M silver nitrate solution until the precipitate turns from yellow to a permanent reddish brown due to the formation of silver chromate.

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

Interferences are bromide and iodide. Also some other metal ion. The following titres were determined four times for each of the chloride standards.

Blank	50 mg/l std	100 mg/l std	200 mg/l std	400 mg/l std	800 mg/l std
0.0	2.80	5.75	11.75	23.65	47.70
0.0	3.10	5.95	12.00	24.15	48.05
0.0	3.25	6.00	11.85	24.30	47.85
0.0	2.95	6.35	12.20	23.85	48.30

For each of the methods.

1. Plot all the data. Is it linear?
2. Draw line of best fit.
3. Calculate the mean ($\bar{x}$), standard deviation (s) and relative standard deviation (RSD) for each standard.

Mean	*Standard deviation*	*Relative standard deviation*
$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$	$s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n}}$	$RSD = \frac{s}{\bar{x}} \times 100\%$

4. Use the graph to determine the concentration for the mean for each standard.
5. Calculate the concentration of chloride for the mean for each of the standards using the details in the procedures.
6. Comment upon the difference between those values determined from the graph and the calculated values.
7. Plot the calculated concentrations for one method against the other.

Spectrophotometric: Mercury (II) Thiocyanate Method

Place a 200 ml aliquot of the water sample into a 250 ml graduated flask, add 2 ml of 0.025 M ammonium iron(III) sulfate in 9 M nitric acid, followed by 2 ml of a saturated solution of mercury(II) thiocyanate in ethanol. After 10 minutes measure the absorbance of the sample solution against the blank in 5-cm cells.

$$2\,Cl^- + Hg(SCN)_2 \rightarrow HgCl_2 + 2[Fe(SCN)]^{2+}$$

The following absorbances were determined four times for each of the 50, 100, 200, 400 and 800 mg/l chloride standards.

Blank	50 mg/l std	100 mg/l std	200 mg/l std	400 mg/l std	800 mg/l std
0.008	0.136	0.231	0.407	0.822	1.496
0.002	0.129	0.245	0.428	0.868	1.443
0.004	0.141	0.256	0.437	0.830	1.452
0.011	0.120	0.222	0.454	0.845	1.474

1. Plot all the data. Is it linear?
2. Draw line of best fit.
3. Calculate the mean, standard deviation (s) and relative standard deviation (RSD) for each standard.
4. Use the graph to determine the concentration for the mean for each standard.
5. Plot the values taken from the graph against the values determined for the gravimetric method by calculation.
6. Comment on the graphs of the three methods.
7. Discuss which method you would employ in the Environmental Monitoring Laboratory.

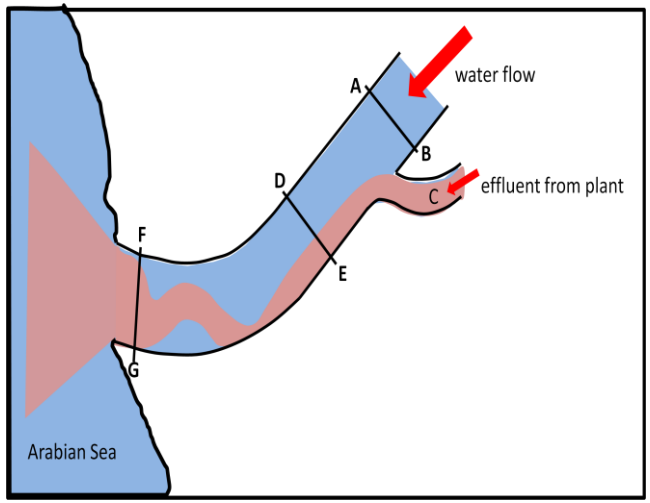
NOTES

Problem Solving

In setting up the Environment Monitoring Laboratory for Titan Industries, the following need to be considered.

Sampling

Titan Industries will produce titanium dioxide by the chloride process. will be a constant discharge of liquid into the local river and coastal waters. There is a potential for chloride discharge which must be kept below court-ordered limits.



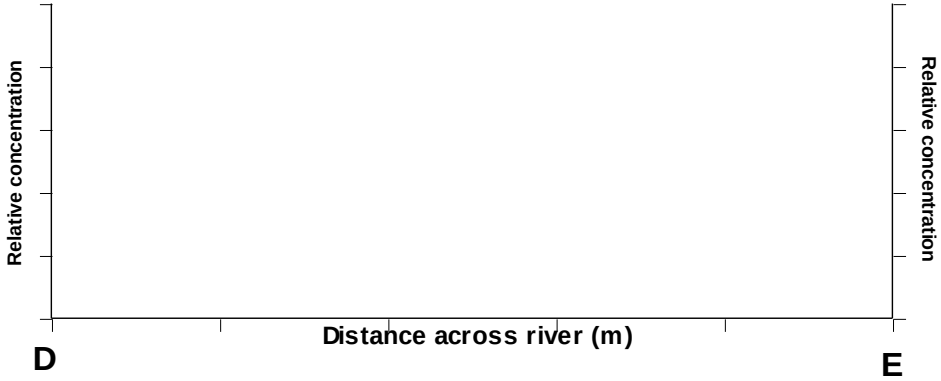
1. Where would you sample so that you could gauge the base levels for the river?
   a. Downstream before the bend (D-E)
   b. At the Outflow pipe (C)
   c. Downstream after the bend in the river (F-G)
   d. Up-stream (A-B)

2. Where would you sample the outflow?
   a. Up-stream (A-B)
   b. Downstream after the bend in the river (F-G)
   c. At the Outflow pipe (C)
   d. Downstream before the bend (D-E)

3. Where would you get a direct measure of concentration in the river?
   a. Downstream after the bend in the river (F-G)
   b. Up-stream (A-B)
   c. At the Outflow pipe (C)
   d. Downstream before the bend (D-E)

4. Could sampling point C be related to the final concentration in the river? If so what further information would be required in order to make an estimate?

5. Draw a profile of the pollution levels at point D-E



6. If you only sampled at F-G, would you be certain of the location of the discharge point?

Converting Units

Many of the problems with environmental monitoring concern dealing with different units and attempting to explain the results to non-chemists.

7. These are some results from various analyses that require conversion for a report you are preparing for Titan Industries.

parts per billion (ppb)	parts per million (ppm)	grams per litre (g/l)	% weight per volume (w/v)
2.3×10^{6} ppb	2.3×10^{3} ppm		
	0.9 ppm	9×10^{-4} g/l	
212 ppb			2.12×10^{-5} % w/v
	4.1×10^{4} ppm		4.1% w/v
		1.031 g/l	0.1031% w/v
1.2×10^{5} ppb		0.12 g/l	

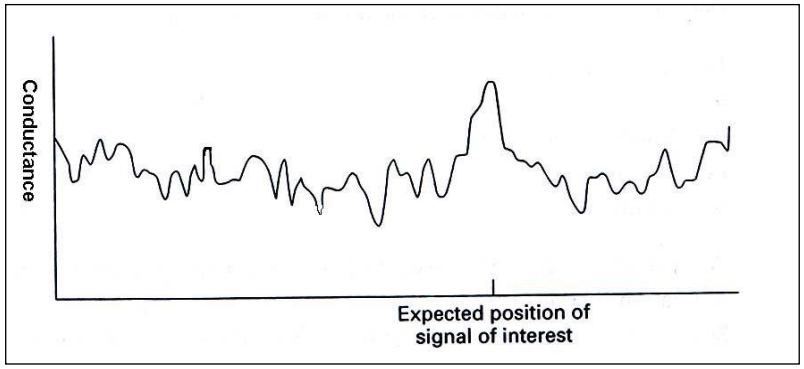
Limit of Detection

Limit of detection and limit of determination are often confused especially by the non-analytical chemist. They are defined in terms of the signal to noise ration (S/N). The former is always larger than the latter.

9. What is the definition of Limit of Detection?
    a. Ten times the standard deviation of the noise.
    b. Three times the standard deviation of the noise.
    c. Can just be distinguished from the noise of the blank.

10. What is a sensible Limit of Determination?
    a. Ten times the standard deviation of the noise.
    b. Three times the standard deviation of the noise.
    c. Can just be distinguished from the noise of the blank.

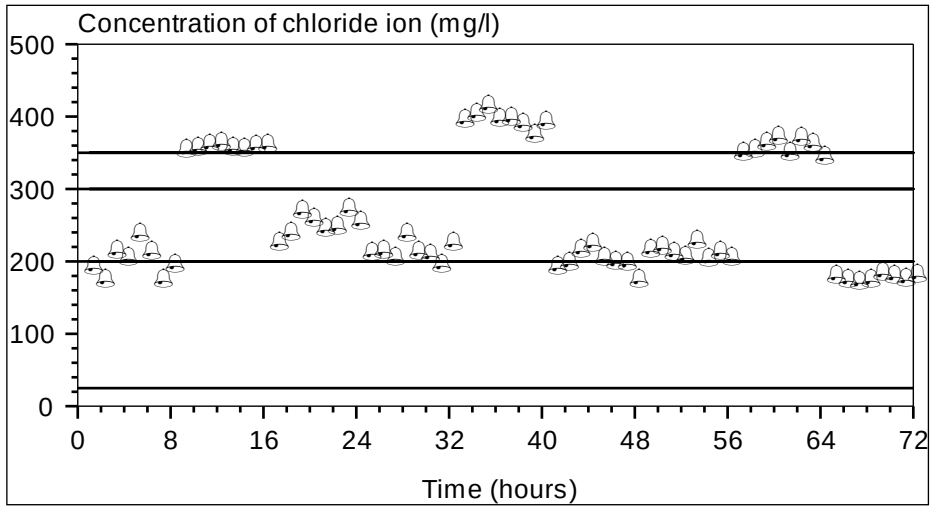
11. A chromatograph from the ion chromatography of chloride in the effluent stream is shown below.



    a. Do you think there is any chloride present in the effluent?
    b. Would you be willing to quantify that amount of chloride present?
    c. How would you choose the base line?

Control Chart

12. A Shewart control chart for chloride ion in effluent was produced over a three-day period by another Titan Industries plant.



    a. Suggest possible reasons for the nature of the plotted results.
    b. How could you argue that you are not above the critical value of 350 mg/l?

Costing

Your line manager has asked you to consider supplying contract analytical services to different customers.

13. Give two examples of a fixed cost within an analytical laboratory?

14. Give two examples of variable costs with the analytical laboratory.

15. What would you take into account when setting a realistic price to cover your costs for a single analysis of Cl^- in effluent by ion chromatography?

16. How would you justify charging a different price if you were providing a regular analysis of Cl^- in effluent by IC for an external customer?

17. Could you justify charging a different price to a customer within Titan Industries for Cl^- in effluent by ion chromatography?

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