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ACID EFFECTS IN THE COLD VAPOUR ATOMIC ABSORPTION SPECTROMETRIC DETERMINATION OF MERCURY IN BIOLOGICAL AND ENVIRONMENTAL MATERIALS

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Abstract: The influences from four major acids (HCl, HNO₃, H₂SO₄ and HClO₄) and their mixtures, simulated as residual acids, on the mercury response in standard solutions of HgCl₂ were studied. It was found that the concentration of HCl and HNO₃ had little or no influence on the mercury response, whereas the presence of H₂SO₄ significantly increases the mercury response. The presence of small amounts (\leq 4 ml) of HClO₄ decreased the mercury absorbance reading, but the response increased with further addition of the acid. Nitric acid mixed with HClO₄ improved the mercury response slightly, but the addition of H₂SO₄ caused greater improvements. The nitric and sulphuric acid digestion mixture has an advantage over other mixtures for the determination of total mercury in biological and environmental samples.

Keywords: Cold vapour atomic absorption spectrometry, mercury, residuals acids, interference, biological/environmental materials.

Introduction

The critical step in the measurement of mercury by cold vapour atomic absorption spectrometry (CV-AAS) is the decomposition and subsequent preparation of the sample. The success of the method lies in the preparation of a sample solution containing all the mercury in the divalent form as well as avoiding interferences from the constituents of the solution during the mercury reduction.

The use of strong mineral acids or their mixtures in different proportions is commonly employed for the decomposition of biological and environmental samples at various temperatures for the CV-AAS determination of mercury. The resulting mercury response may be influenced during the decomposition of the sample by acids or acid mixtures in two ways. Firstly, the mercury may be lost during the sample decomposition, preparation and preservation [1-3, 7] and/or secondly, the components of the sample solution, especially residual acids, may interfere with the mercury determination [4-6]. The latter may further be classified into two categories:

- (i) the residual acids may create a suitable acidic environment in which ions and molecules produced as a result of the decomposition of sample may interfere with the mercury determination [4] and/or
- (ii) the residual acid(s) from the decomposition step may interfere with the mercury measurement by forming complexes with Hg^{2+} in the digest that may not allow the reduction of Hg^{2+} to Hg^{0} by stannous chloride in the CV-AAS technique [4-6].

Several attempts have been made to minimise the loss of mercury from the sample during sample digestion, preparation and preservation [1-3, 7], as well as on the interference due to the presence of excessive quantities of other metal ions [8-11]. However, very little attention has been paid to the effect of residual acids on the mercury response. Moreover, previous studies in this area have used different proportions and concentrations of acids, and therefore the effects of different acids could

not be compared. The residual acids could be part of the decomposition step or are added along with other reagents; for example, addition of HCl along with the stannous chloride, the reducing agent used in the study. HCl is therefore not a part of the decomposition step, but is added after decomposition of the sample. Similarly, H₂SO₄ if added in the beginning of the sample decomposition step, often results in charring that causes loss of mercury from the sample. Its post-addition, after decomposition of sample with HNO₃, is preferred. Perchloric acid is a strong oxidising acid. It is not often used in the decomposition of samples because its fumes form explosive compounds with environmental materials. However, it is safe to use if a special fumehood is available. These conditions highlight the importance of studying the effects of pre- and post- addition of the component acids. The available information on the interference of residual acid mixtures on the CV-AAS determination of mercury is rather limited. Therefore, there is a need for further investigation.

The aim of this study was to investigate the interference of individual residual acids (HNO₃, HCl, H_2SO_4 and HClO₄) as well as of their combinations on the mercury response of a standard solution and, biological and environmental samples. In order to avoid the major problems associated with the presence of large number of other ions and molecules, standard solutions of $HgCl_2$ were used to examine the interference effect of the residual acids on the mercury response by CV-AAS.

Experimental

Reagents and Standards

All reagents used in this study were of analytical grade. The mercury stock solution (1 g/l) was prepared daily by dissolving the appropriate amount of HgCl₂ in water. A mercury standard solution (1 mg/l) was prepared by diluting the above stock solution with milli-Q (MQ) Water. Stannous chloride solution (30% w/v) was prepared daily by dissolving the appropriate amount in 20% (v/v) hydrochloric acid and stabilised by the addition of a piece of tin. Concentrated sulphuric acid, nitric acid, hydrochloric acid and perchloric acid were diluted to solutions of equal normality (10.5 N). Milli-Q water was used for preparing solutions and diluting acids.

Instrumentation, Glassware and Procedure

CV-AAS measurements were performed on a Varian Spectra 20 atomic absorption spectrometer operated in the double beam mode. The conditions employed for the measurements were: wavelength, 253.7 nm; slit width 0.5 nm, lamp current 0.3 mA.

All glassware and plastic containers were soaked in nitric acid (2M) for at least 24 hours and rinsed 4-5 times with Milli-Q water prior to use.

Standard reference materials (SRM)

Prawn (Agal-3) and Bovine liver (Agal-20) reference materials were obtained from the Australian Government Analytical Laboratories, Pymble, NSW, Australia.

Procedure

CV-AAS Measurement

A 100 ml Erlenmeyer flask containing 20 ml of a solution prepared by adding the appropriate amount of acid or acid mixtures and $0.150 \ \mu g$ of mercury as mercury (II) chloride, was connected to the mercury vapour generation system, one ml of stannous chloride was added and the contents of the flask were stirred with a magnetic stirrer at maximum speed for 3 minutes. The resulting mercury vapour was displaced from the flask to the mercury cell by the water displacement method at a rate of 10 ml/s [13]. After recording the mercury response, the cell was flushed out with instrumental grade nitrogen.

Method

A 0.5 g prawn sample (or 0.2 g bovine liver or 0.5 g lake sediment) was weighed into a dry 100 ml conical flask. The sample was digested under two conditions: pre- and post-addition of digestion mixtures For the pre-addition, 3 ml concentrated HNO₃ was added to the flask containing solid sample and the contents were heated at 90°C for 10 minutes to avoid charring as well as the vigorous reaction of organic matter with other acids. One millilitre of concentrated sulphuric acid (and/or 1.5 ml of 70% perchloric acid) was then added and the loosely stopped flask was further heated for 80 minutes at 90°C. During post-addition, the sample was digested in nitric acid at 90°C for 90 minutes and then one millilitre of concentrated sulphuric acid (and/or 1.5 ml of 70% perchloric acid) was added. The sample was also digested using nitric acid without addition of sulphuric acid and/or perchloric acid giving rise a pre-addition condition only; which was also the case when standard solution were used to study the acids' interferences. The flask was cooled to room temperature. The stopper and the sides of the flask were rinsed with MQ water and the final volume was made up to 20 ml. The flask was used for CV-AAS measurement of mercury.





Experimental

Interference from a single acid

Figure 1 shows the effect of increasing addition of individuals acids on the size of the mercury response for the standard solution of $HgCl_2$ in water. The addition of $HClO_4$ up to 4 ml suppressed the mercury response significantly, whereas further addition up to 8 ml of $HClO_4$ increased the mercury response to a higher value that was obtained without the addition of $HClO_4$. Hence, the maximum signal for mercury can only be obtained in the complete absence or the presence of at least 8 ml of 10.5 N $HClO_4$ (equivalent to 4.2 N $HClO_4$ in the solution used to measure the mercury response). Lower concentrations of $HClO_4$ will suppress the mercury response by up to 30% when 4 ml of 10.5 N perchloric acid is present in the solution.

The addition of sulphuric acid increased the mercury response. The increase in the mercury response as a result of the initial addition of H_2SO_4 was significantly smaller than the decrease caused by the initial addition of $HClO_4$. This indicates that a slight decrease in the concentration of $HClO_4$, when 4 ml or less is used, will produce a significantly higher signal and hence a higher total mercury concentration in the same sample.

Figure1 also shows that the addition of HCl and HNO₃ respectively had only a slight effect on the mercury response. The initial addition of HNO₃ increased the mercury response followed by a slight decrease with further additions of HNO₃. Thus, a variation in the residual amount of HNO₃ will have little effect on the size of the mercury response, whereas the increasing addition of HCl will cause a slight decrease in the mercury response. These effects were similar to those reported earlier [5]. In contrast, the variation in the residual amounts of H_2SO_4 and $HClO_4$ will tend to have a more significant influence on the mercury response. Acids can influence the partition coefficient of elements between the vapour and the solution [4]. It appears that the addition of H_2SO_4 increased the size of the mercury response by increasing the partition coefficient of the element between the vapour and the solution. The addition of HCl and HNO₃ seems to have little effect on the partition coefficient of mercury between its vapour and the solution. From this experiment, it appears that addition of up to 4 ml of 10.5 N HClO₄ decreased the partition coefficient, which was improved with further addition of HClO₄.

The data reported in Figure 1 were obtained using acid solutions of equal normality, therefore it was possible to reorganize the data to evaluate the effect of pH and anion type on the mercury response. The effects of pH and anions on the mercury response are shown in Figure 2. Since the acids used in this study were of equal normality, the H^+ concentration for a fixed volume reflected by each curve in Figure 2 is constant. Hence, the observed individual variation in the mercury response may be attributed to the anions. However, the variation in response for each acid with increasing volume (especially at 2 ml, 4 ml or 8 ml) may be attributed to both H^+ and A^- concentrations. The presence of chloride and nitrate ions has little effect on the mercury response, whereas the presence of sulphate ions increased the mercury response while perchlorate ions decreased the response.



Figure 2: pH and anionic interference on the mercury response (0.15 µg of Hg)

It is evident therefore that at a particular H^+ concentration, it is the nature of the anion that seems to determine the partition coefficient of mercury between its solution and the vapour, and hence, the resulting mercury absorbance. A strong correlation between the following order of the resulting mercury salts (eg. HgSO₄ > HgCl₂ = HgNO₃ > Hg(ClO₄)₂) in solution and the mercury response was observed. This trend is consistent with the available solubility and instability data about these four salts [13]. Mercury perchlorate and Mercuric nitrate are highly soluble, Mercuric chloride is less soluble (7.3 g/100g) and mercuric sulphate is least soluble (0.04g/100g). Since the digestion of biological and environmental samples mostly involves the use of more than one acid, the above discussed interference pattern may change when more than one residual anion is present in the final solution. For that reason

the effects of the most widely used mixtures of HNO_3 with H_2SO_4 or $HClO_4$ were further investigated with the standard solutions.

Interference from a mixture of two acids

Figure 3 demonstrates the effect of increasing amounts of H_2SO_4 in a H_2SO_4 /HNO₃ mixture. There was no difference in the mercury response when addition of up to 6 ml of 10.5N sulphuric acid was made to the mercury standard solution containing 2 or 4 ml of nitric acid. However, further addition of sulphuric acid into a solution containing 2 ml of nitric acid produced a significantly higher response than that containing 4 ml of nitric acid. An increase in the mercury response with increased addition of sulphuric acid reported here is consistent with other studies [4, 6]. The curves in Figure 3 are very similar to those shown in Figure 1 for H_2SO_4 and HNO₃ when used individually.

Figure 3: Effect of increasing amounts of H_2SO_4 on the mercury (0.15 µg Hg) response in the presence of fixed amounts of HNO₃ (2 ml and 4 ml)



Figure 4 shows the effect of the addition of $HClO_4$ on the mercury response in a solution containing HNO_3 or H_2SO_4 . The curves are similar to the one obtained for $HClO_4$ alone. However, the presence of HNO_3 or H_2SO_4 along with $HClO_4$ reduced the suppressive effect of perchloric acid on the mercury response. The efficiency of HNO_3 in increasing the mercury response by reducing the suppressive effect of $HClO_4$ was evident when 4 ml or more of $HClO_4$ was present.

The effect of increasing addition of $HClO_4$ to a standard solution of mercury containing 2 ml H_2SO_4 (Figure 4) was different to that obtained with 2 ml HNO_3 . The addition of 2 ml of H_2SO_4 to a mercury standard solution at various concentrations of $HClO_4$ increased the mercury response almost equally at each $HClO_4$ concentration, which was significantly higher than the increase in mercury response obtained with the addition of 2 ml of HNO_3 . The above results show that the presence of H_2SO_4 as residual acid along with $HClO_4$ partially compensate for the suppressive effect of $HClO_4$ on the mercury response. This finding provided a basis for further investigation of the effect of sulphuric acid in the nitric and perchloric acid digestion mixture even though a perchloric and sulphuric acid mixture is not normally used for sample decomposition. It is interesting to identify the effect of changes in residual H_2SO_4 concentrations on the mercury response in the presence of a fixed amount of $HClO_4$.





Figure 5: Effect on increasing acid or an acid mixture in the presence of 2 ml of perchloric acid on mercury response (0.15 µg Hg, acids 10.5 N)



Figure 5 shows the effect of increasing additions of HNO_3/H_2SO_4 mixture and H_2SO_4 to the mercury solution containing 2 ml of $HClO_4$. Addition of 2 ml of H_2SO_4 increased the mercury response by compensating partially for the suppression caused by 2 ml of $HClO_4$. However, the compensation was only 70% of the maximum loss in sensitivity caused by the presence of perchloric acid, thus indicating a net loss in sensitivity in the presence of $HClO_4$. Further addition of H_2SO_4 improved the mercury response slightly indicating that 2 ml of $10.5N H_2SO_4$ (= 0.6 ml of concentrated H_2SO_4) should at least be present in 20 ml of the solution used for the mercury measurement when $HClO_4$ is a component of the digestion mixture. $HClO_4$ is usually added to digestion mixtures containing HNO_3 and H_2SO_4 for the decomposition of biological and environmental samples and, hence, it is useful to investigate the effect of three residual acids on the mercury response.

Interference from mixture of three acids

The effect of the addition of equinormal and equivolume mixtures of H₂SO₄ and HNO₃ on the mercury response in the presence of 2 ml of 10.5N HClO₄ is also demonstrated in Figure 5. The selection of equinormal and equivolume conditions for HNO3 and H2SO4 mixture was based on the commonly employed mixture of these acids as a digestion mixture. It was found that in most studies [1, 2, 6] a mixture of concentrated HNO₃ and H₂SO₄ in a 2:1 volume ratio was used. A volume of 2 ml of perchloric acid was selected to keep it consistent with the volume used in the previously described experiment to compare the results obtained using a HNO₃ and H₂SO₄ mixture with that of H₂SO₄ alone. The effect of adding a nitric acid and sulphuric acid mixture was different from the addition of H₂SO₄ during the first addition (2 ml) of the acid mixture, but similar thereafter. The addition of 2 ml of equinormal acid mixture (1 ml of each H₂SO₄ and HNO₃) did not improve the mercury response significantly when compared with the mercury response in presence of HClO₄ alone. This indicated that 1.0 ml of 10.5 N H₂SO₄ (= 0.3 ml) was not adequate for the stabilisation of mercury response in the presence of a residual acid mixture containing three acids. However, the addition of 4 ml of a HNO₃ and H₂SO₄ mixture (2 ml each) increased the mercury response to almost same level that was obtained in the presence of 2 ml of H₂SO₄ alone and thus partially compensates for the loss of mercury response due to HClO₄ interference. Further addition of the HNO₃ and H₂SO₄ acid mixture improved the mercury response slightly, indicating an almost steady state. Moreover, the mercury response in the presence of nitric acid and sulphuric acid was lower than the one obtained for sulphuric acid alone. This experiment further supports the finding that in the presence of residual HClO₄ at least 2 ml of 10.5 N H₂SO₄ (0.6 ml concentrated H₂SO₄) should at least be present in the solution, to almost completely neutralise the suppressive effect of HClO₄.

Despite mixing different acids with $HClO_4$ in different proportions, it was not possible to compensate completely for the suppression of the mercury response unless large volumes of $HClO_4$ and/or H_2SO_4 were used. The use of such large volumes is not advisable because of the exothermic and explosive nature of these acids.

The effect of different decomposition acids on the determination of mercury in a standard reference material was studied under the conditions that involved digestion of the sample using nitric acid alone, as well as using acid mixtures that involved addition of the component acids (sulphuric acid, or perchloric acid or their mixture) to nitric acid under pre- and post addition conditions. The pre- and post-addition conditions are explained in methodology section. To study these effects, four calibration curves were drawn using these mixtures. It is clear from the results in Table 1, that the use of nitric and sulphuric acid, nitric and perchloric acid, nitric, sulphuric and perchloric acid mixtures increased the recovery of mercury in the prawn (Agal-3) reference material under pre- and post-conditions when compared to the recovery obtained using nitric acid only. Nitric and perchloric acid mixtures gave recovery values that are above the reference value range indicating some unknown interference from the perchloric acid. It appears that a part of the perchloric acid was used up during the digestion of sample and another part was lost due to decomposition of perchloric acid, as around 100°C perchloric acid is decomposed quickly, and hence its concentration decreased. A decrease in 2ml per 20 ml of solution in the testing flask, will increase the mercury response as demonstrated on the left side of its curve in Figure 1, it results in an increase in the mercury response. Addition of H₂SO₄ to the nitric and perchloric acid digestion mixture decreased the interference due to perchloric acid and the total concentration of mercury in the prawn was again within the limits of the reference value. The boiling point of sulphuric acid is 330°C therefore it will not be lost due to evaporation when the sample is digested at 90°C. A comparison of the total mercury concentrations in the prawn reference material obtained under pre and post conditions shows that the mercury value under pre condition was higher than for post condition. This indicates that the concentration of perchloric acid was effected during the digestion process as a result of either consumption, decomposition, evaporation or all three. However, no difference in the total mercury recovery in the reference sample was observed when a nitric and sulphuric acid mixture was used as the decomposition mixture under pre- and post-condition. This indicated that sulphuric acid may be added at any time during the digestion process. This hypothesis was tested by using pre- and post-addition in the Bovine liver and lake sediments samples.

| Sample | Reference | Component acid | Pre- Condition | Post- Condition |
|----------------|---------------|--|----------------------------|----------------------------|
| | value(µg/g) | added to HNO ₃ | (Mean \pm SD; μ g/g) | (Mean \pm SD; μ g/g) |
| Prawn | 0.15 ± 0.03 | | 0.146 ± 0.009 | |
| Prawn | | H_2SO_4 | 0.159 ± 0.002 | 0.159 ± 0.004 |
| Prawn | | HClO ₄ | 0.182 ± 0.005 | 0.176 ± 0.007 |
| Prawn | | H ₂ SO ₄ & HClO ₄ | 0.171 ± 0.002 | 0.163 ± 0.003 |
| Bovine Liver | 0.67 ± 0.07 | | 0.674 ± 0.012 | |
| Bovine Liver | | H_2SO_4 | 0.690 ± 0.013 | 0.689 ± 0.018 |
| Lake sediments | 5 Unknown | | 0.118 ± 0.001 | |
| Lake sediments | 8 | H_2SO_4 | 0.136 ± 0.004 | 0.134 ± 0.003 |

Table 1: Mean mercury determined in prawn, and bovine liver (reference materials) as well as in the lake sediment using pre- and post-addition of component acids for sample digestion(n= 3)

Table 1 also shows the effect of pre- and post-addition of sulphuric acid on the mercury concentration in bovine liver and lake sediment. Evidently, the post-addition of sulphuric acid after predigestion with HNO₃ gave similar results to a sample digested with the mixture $HNO_3 - H_2SO_4$. The use of the HNO₃ digestion is advantageous in reducing sample charring which often occurs with the HNO_3 and H_2SO_4 digestion mixture. The addition of sulphuric acid to the HNO_3 digested samples therefore provides a simple means of improving the sensitivity for mercury determination. In effect this provides an excellent basis for accomplishing both optimum decomposition and analytical conditions. A nitric and sulphuric acid decomposition mixture (with post addition of sulphuric acid) had an advantage over the other acid or acids mixtures for the determination of total mercury in biological and environmental samples.

Conclusion

The concentration and the nature of the acid(s) in a solution used for mercury measurement can influence the mercury response significantly. Moreover, due to the anions interfering significantly with the mercury response, it was found that the HCl and HNO₃ concentrations have little influence on the mercury response, whereas, H_2SO_4 significantly increased the response, while HClO₄ caused a significant suppression. The presence of up to 4 ml of 10.5N HClO₄ in 20 ml of the final solution decreased and further addition of up to 8 ml of 10.5N HClO₄ increased the mercury response. The mixture of acids produced a mercury response between the range for individual acids. Nitric acid mixed with HClO₄ improved the mercury response slightly, however H_2SO_4 cause the greatest improvement. The use of perchloric acid in the decomposition of biological and environmental materials for mercury determination should be avoided not only because of its explosive nature, but also due to its interference. If it is necessary to use perchloric acid, the addition of about 1 ml of concentrated H_2SO_4 as well is recommended. The nitric and sulphuric acid digestion mixture has distinct advantages over other mixtures.

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A QUALITATIVE ASSESSMENT OF AN URBAN AIR POLLUTION MONITORING NETWORK AND ITS SPECIFIC LIMITATIONS

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Abstract: The aim was to determine the effect of wind on the measurement of pollution levels and highlight the extent of non detection due to pollutants being carried away from the monitoring sites. Data recorded by the Environmental Protection Authority (EPA), Queensland at 4 monitoring stations in the industrial region of Gladstone was used for analyzing the effect of wind on detected levels of pollution. Plots of measured NO_x levels and wind speeds at different wind directions were analyzed to gain an understanding of the trend in detection, the likely spread of the pollutants and the extent to which pollution may be undetected. The detection capability of a monitoring station for detecting NO_x from known sources in the vicinity at certain wind directions and degree of pollution introduced by sources in the same wind directions were defined and estimated. The detection capability at the sites over a 10° interval varied from 1.5 - 8.5%. The degree of pollution introduced by different sources varied from 0.5 -14% over the same interval. This provided information on the extent to which high levels of pollution may not be detected by a monitoring network due to dispersion in directions with low detection capability and therefore not reported, being a limitation of the monitoring network to provide complete information on spatial distribution in the area. Similar limitations exist with most urban monitoring networks and need to be considered by the public, health authorities and environmental policy makers when assessing risk of population exposure and environmental damage.

The use of inverse models to determine source emissions and use of dispersion models to determine levels at locations where there are no monitoring stations to gain a better understanding of overall spatial distribution have been proposed.

Introduction

It is widely accepted that air pollution could have dramatic effects on natural ecosystems, climate, health of people and other animal species. As a result there is a need to monitor the pollutants in the atmosphere and set maximum permissible limits to the different pollutants based on their toxic nature. When the maximum permissible limits are exceeded the monitoring authorities usually report the number of such incidences so that health authorities, environmental policy makers and regulatory authorities become aware of the situation. Due to wind effects, monitoring stations may be unable to detect high levels of pollutants in the atmosphere especially when they are being dispersed away from the station. In such situations maximum permissible levels may be exceeded at some locations in the region but may not be reported due to non-detection. The environment and health of the people may still be affected, as well as lead to incorrect information on the status of air pollution being passed on to environmental policy makers and regulatory authorities.

A monitoring network must be able to provide sufficient information on air quality for regulatory authorities to assess compliance, identify polluting sources, observe pollution trends in urban and non-urban areas, judge their effects on the population and the environment and take emergency control measures when necessary. Usually the information from monitoring networks is used for determination of maximum concentration within spatial domains, assess population exposure, establish background levels, analysis of temporal trends and establish source–detector relationship for particular sources which have an impact on air quality in the region (Demerjian 2000). Designing a network to

satisfy all the above objectives is not a simple task. Sites for monitoring stations are usually chosen considering location of sources, meteorological conditions and terrain. For practical air quality sampling the statistical methods used are systematic sampling, judgmental sampling and geostatistical sampling (Chow et al 2002). There are many publications on design of monitoring networks (Smith and Egan 1979, Nakamori et al 1979, Munn 1981, Modak and Lohani 1985, Kainuma et al 1990). The network design must include essential features to evaluate performance and provide feedback to correct limitations (Demerjian 2000). The typical network will be in an urban area with multiple sources and high population density. It provides information on exact pollutant concentrations and temporal variability at the monitoring networks. Therefore there is a need for quantitative assessment of monitoring networks to gain an understanding of their limitations and apply other measures to overcome these limitations and gain a better understanding of spatial distribution over the region.

The focus of this study is on the NO_x concentration levels recorded at 4 different monitoring stations in the Gladstone region of Queensland, Australia. As per National Pollutant Inventory (NPI) Emissions Report, Fig. 1(a) shows that this region has significant number of industries such as power generation, alumina smelter and refinery, chemical processing, shale oil etc. More capital investment for further industrial development has been planned for this region (Air Quality Report, EPA Qld 2000). There is a population of nearly 30,000 people who live in the proximity of the industrial sites. As shown in Fig. 1(b), the Queensland Environmental Protection Authority (EPA) has monitoring stations at South Gladstone, Barney Point, Targinie, Mt Miller, Ticor Hill and Clinton. SO₂ (Barney Point, Targinie, Mt Miller, Ticor Hill, Clinton), NO₂ (Barney Point, Targinie, South Gladstone, Mt Miller, Ticor Hill, Clinton), and visibility reducing particles of range 0.1-2.5 μ m (Barney Point, Targinie) are monitored at these sites at half hourly intervals. The locations of these monitoring sites in relation to the possible polluting sources have been transposed to Fig. 1(a) in abbreviated form (BP- Barney point, SG-South Gladstone, T-Targinie, C-Clinton). Annual statistical summary of these results is available at the Queensland EPA website.

Figure 1: Industries and monitoring stations in the Gladstone region.



(a) Industries in Gladstone region



(b) Monitoring stations in Gladstone region

The aim of this analysis was to identify the sources of pollution and check the extent to which the monitoring network could detect the emissions from these sources at all times under different wind directions. This is a basic study on the effect of wind direction on the NO_x levels recorded at the Barney point, South Gladstone, Targinie and Clinton monitoring stations over the 1996-2001 period to identify the sources of NO_x pollution, the direction of spread and the proportion detected. The polluting nature of the sources and the detecting capability of the stations have been assessed to gain an understanding of the limitations of the monitoring network to provide a realistic view of the spatial distribution of NO_x in the region.

Data

Queensland EPA maintains a network of monitoring stations in the industrial region of Gladstone. Details of the network are given in the Queensland Air NEPM monitoring plan. The monitoring stations are equipped to carry out measurements on gaseous and particle pollutant levels as well as meteorological parameters. The equipment is calibrated and maintained by technical staff from EPA. All measurements are checked and validated by the EPA staff. The NO_x levels measured at half hourly intervals were used for this study. The data was obtained on comma delimited Excel spreadsheets for the analysis. A dataset was constructed as an Excel spreadsheet with monitoring sites as rows, half hourly wind direction, wind speed and NO_x concentration levels (pphm) as columns for the analysis.

Method

The half hourly recordings of NO_x levels at the different monitoring stations were plotted against wind direction at the time of recording on a yearly basis to identify the wind direction at which higher levels of NO_x was being detected on a regular basis and the location of the NO_x sources in relation to the stations. Wind speed was plotted against wind direction to gain an understanding of the wind speed at

different wind directions and its effect on NO_x levels recorded. The mean NO_x levels were determined at these identified wind directions and compared with the overall mean levels. The frequency distribution of wind direction was obtained at each of the monitoring stations to gain an over view of the dispersion of NO_x in the region.

A measure of ability to detect NO_x with wind assistance was estimated for wind directions at which maximum permissible levels (16 pphm) were exceeded or levels much higher than the usual background of 3 pphm was being measured on a regular basis. The measure of detection capability was considered as equal to the ratio:

No. of measurements within selected range of wind directions All wind direction measurements $0-360^{\circ}$ range

The number of NO_x levels at a monitoring station in a particular wind direction above twice the background expressed as a proportion of all the measurements in that direction was taken as a measure of pollution from an identified source or group of sources.

Proportion of high NO_x emissions is equal to the ratio:

No. of recordings above twice background in particular wind direction All recordings in the same wind direction

The proportion of high NO_x emissions by a single source or group of sources was estimated based on the emissions above twice background levels measured in the selected wind directions.

The number of incidences when NO_x levels exceeded maximum permissible concentrations was plotted against wind direction for comparing with the capability of detection and also these levels were plotted against wind speed to determine its effect on NO_x levels recorded.

Results and Discussion

NO_X levels at different wind directions

The variation of NO_x with wind direction at the site during time of measurement for Barney point, South Gladstone, Targinie and Clinton stations for 2001 is shown in Figures 2(a)-(d) respectively. The levels shown for 0^0 wind direction are the measurements carried out at zero wind velocity under near perfect diffusion conditions. **Figure 2:** Variation of NOx with wind direction at different stations. (a) Barney Point



(b) South Gladstone





(d) Clinton



Fig. 2 shows that most of the NO_x measurements at these stations were less than 3 pphm at most times and this was considered as the background level for the purpose of this study. Fig. 2(a) for Barney point station shows a clear peak for NO_x levels at a wind direction of 107^{0} and levels much higher than the usual background at approximately 194^{0} , 258^{0} , 272^{0} and 332^{0} . Similarly Fig. 2(b) for South Gladstone station showed a clear peak as well as similar high levels at more or less the same wind directions. In addition there appears to be high levels above background detected at 304^{0} . Fig. 2(c) for the Targinie station showed a wide peak at approximately 97^{0} and Fig. 2(d) for the Clinton station showed peaks at approximately 57^{0} , 196^{0} and 358^{0} respectively. The clear peaks in Figs. 2(a) and 2(b) 18

are most likely as a result of emission from a group of two sources located southeast of this station close to each other as shown in Fig. 1(a), aligned to the monitoring station in the same direction as the prevailing wind from the southeast at the time of measurement. The high levels observed at Barney point and South Gladstone station for other wind directions as mentioned above, may be originating from sources located from southwest to northwest of these stations (Fig. 1(a) and Fig. 1(b)). The wide peaks seen in Fig. 2(c) for the Targinie station could be as a result of emissions from the sources of NO_x located southeast of this station aligned to the monitoring station at angles close to the direction of the prevailing wind at the time of measurement. Similarly in Fig. 2(d) the wide peaks centered at 196° could be emissions from sources located southwest of this station at Clinton (Fig. 1(a)), while the high levels observed at 57° and 358° could be from sources located north and northeast of this station.

From the peaks and high levels seen in Fig. 2 it is clear that there are sources with high NO_x emissions in the region, which can be detected only at certain wind directions. When there was no wind the levels detected were always less than approximately 8 pphm (parts per hundred million) as shown by points lying on the x-axis in Fig. 2(a)-(d). These levels represent recordings under near perfect diffusion conditions with no wind assistance. In some instances the NO_x levels measured at certain wind directions were above the maximum permissible level of 16 pphm specified by the National Health and Medical Research Council (NHMRC).

The wind speed at the wind directions mentioned above needed to be analyzed in order to gain a better understanding of the overall impact of wind on detection of NO_x in this region. Figs. 3 (a)-(d) show wind speed at different wind directions at the same stations mentioned above.

Figure 3: Wind direction against wind speed. (a) Barney Point









(d) Targinie



All stations showed consistently the prevalence of wind speeds above 4 ms⁻¹(14.4 kmh⁻¹) in the wind directions at which high NO_x levels were detected. Especially the high NO_x levels observed at approximately 100^{0} wind direction at Barney point, South Gladstone and Targinie stations would have been carried to these sites at these wind speeds. Similarly the higher wind speeds observed at the Barney point, South Gladstone and Clinton stations at $300-360^{0}$ and $0-50^{0}$ intervals would have helped detect the higher emissions from sources located northwest of Barney Point and South Gladstone station (Fig. 1(a) and Fig. 2). At instances when the prevailing wind was from the southeast it would have carried away the emissions from the sources located northwest of Clinton station in a northwesterly direction preventing detection of any high emissions. Similarly when the prevailing wind is from the northwest the emissions from sources located southeast of Barney point, South Gladstone and Targinie stations and northeast of Clinton station are carried in a southeast of Barney point.

The wind speeds observed at Barney point, South Gladstone and Clinton stations in the 200-300⁰ interval were not as high compared to the other directions. The high levels that have been detected at these stations due to emissions from sources located west of these stations could be more as a result of dispersion with little or no wind assistance. If there was a greater prevalence of high wind speeds in this direction it may have been possible to detect more instances of higher NO_x levels above what has been already detected at Barney point, South Gladstone and Clinton stations originating from the sources located west of these stations at 225⁰ may have resulted in the emissions from the sources located southeast of this station to be carried away in a northeasterly direction preventing detection.

The observations made in Figs. 2 and 3 show that higher levels of NO_x well above the usual background levels were detected at certain wind directions with the assistance of wind speed. There were a greater number of high level detections in certain wind directions when there were more instances of high wind speed in that particular direction. Similarly due to high wind speeds in other directions carrying the NO_x away from the station, detection was not possible. Therefore high NO_x levels may have existed at certain locations such as southeast and northwest of Barney point, South Gladstone, Clinton stations and southeast of Targinie station without being detected or reported. It is possible that levels exceeding the NHMRC maximum permissible levels may have also existed and not been detected.

Fig. 4(a) and Fig. 4(b) show the measurements at the Barney point station for 1999 and 1997 which appear to be comparable with the measurements for 2001 (Fig. 2(a)). Indicating that the NO_x levels detected at this station is consistent on a yearly basis. This was the case at the other monitoring stations too. This meant that the wind flow patterns and source emissions were consistent from year to year in this region.





(b) Barney Point (1997)



The NOx levels measured within a 5^0 wind direction interval on either side of the clear peaks and high levels identified in Figs. 2(a)-(d) were used to compute mean levels at those wind directions for years 1997-2001. The computed mean levels are shown in Figs. 5(a)-(c). The stations at Targinie and Clinton were established only in 2000 and 2001 and therefore data was unavailable for these stations for the entire period of this study.

Figure 5: Mean NOx levels at different wind directions. (a) Barney Point



(b) South Gladstone





The mean levels shown in Fig. 5(a)-(c) at the selected wind directions were found to be consistently higher than the overall annual mean of 0.5 pphm for the different years. This was a clear indication that there was consistent emission of NO_x from certain sources in the region and this emission could be detected only at certain wind directions. The group of high emission sources could be identified using the wind direction at the time of recording. It is highly likely that at other wind directions the NO_x is being dispersed away from these stations and not being detected. Therefore similar mean levels could exist at other locations in this region where there is no monitoring station for detection. The undetected NO_x levels will contribute towards a higher overall mean for the region. Maximum permissible levels could also be exceeded at other wind directions and not be detected posing a health risk. The extent to which pollution may go undetected needs to be analyzed based on the frequency distribution of wind direction.

Distribution of wind direction

The number of wind direction samples measured at 20° wind direction intervals over an entire year for the four monitoring stations are shown in Fig. 6(a)-6(c).

Figure 6: Distribution of wind direction (a) Barney Point







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(c) Targinie and Clinton



At the Barney point station in Fig. 6(a) most of the wind direction measurements appear to be in the $100-160^{\circ}$ interval, which enabled higher mean levels to be detected in the 107° direction from a source located southeast of this station. Frequent dispersion in the $130-160^{\circ}$ interval would have reduced the levels detected from this source. At South Gladstone station in Fig. 6(b) most of the wind direction measurements were in the $100-160^{\circ}$ range enhancing the chances of detecting the emissions from the sources located southeast of this station. At both stations the frequency of wind direction measurements in the $160-360^{\circ}$ interval is very low and may have significantly reduced the ability to detect pollution from sources located in the region extending from southwest to northwest of these stations. Despite this reduction significantly higher mean levels have been detected at selected wind directions in this range as shown in Figs. 5(a) and 5(b) more as a result of reasonable wind speeds (Fig. 3(a)) helping the dispersion in this direction at the time of detection. This is an indication that emissions from this group of sources could be higher compared to the other groups, but due to less frequent wind from the west it does not get detected as often.

Most of the wind direction measurements at Targinie were in the $60-160^{\circ}$ range and responsible for the wide peak seen in the same direction in Fig. 2(c). This increased frequency enabled detection of NO_x from sources located southeast of this station (Fig. 1(a)). The frequency of wind direction at

Clinton in Fig. 6(c) showed moderately higher frequency in the $40-160^{\circ}$ interval resulting in the peak for NO_x at 57[°] and much higher frequency in the 180-220[°] resulting in the wide peak centered at 196[°] direction (Fig. 2(d)). These peaks indicate emissions from sources located northeast and southwest of this station, which was detectable due to the higher frequency of wind in these directions.

A close analysis of frequency of wind direction in Fig. 6, wind speed in Fig. 3 and NO_x levels detected in Fig. 2 show that the most likely direction for dispersion of NO_x emissions from sources in this region is expected to be in the northwesterly direction. As a result NO_x emissions from sources lying northwest of Barney point and South Gladstone stations, and west and northeast of Clinton station may have a low chance of detection, which is a limitation of this monitoring network.

Moderately high frequencies for wind direction were also observed at Barney point, South Gladstone and Clinton stations in the $0-60^{\circ}$ interval coupled with wind speeds in the $0-5 \text{ ms}^{-1}$ range. This may have caused dispersion in the southwesterly direction which has been detected at these stations and show as minor peaks in Figs. 2(a), (b) and (d).

The number of high NO_x levels that could be detected from a source was more dependent on the frequency of wind direction that is aligned with the source and monitoring station than the wind speed in that direction. To gain a measure of the ability of a monitoring station to detect NO_x , the number of wind direction measurements at a selected wind direction interval (where higher NO_x levels were recorded) was determined as a fraction of all wind direction measurements.

Measure of detection capability

For this purpose the NO_x measurements recorded at Barney point, South Gladstone, Targinie and Clinton for 2001 (shown in Figs. 2(a) - (d)) were used as a guide to select the wind directions at which high NO_x levels were detected. The results computed for the selected wind directions for the period 1997-2001 for Barney point, South Gladstone, Targinie and Clinton stations are shown in Figs. 7(a)-(c).

Figure 7: Detection capability at different wind directions.







(c) Targinie and Gladstone



The detection capability at Barney point and South Gladstone was higher at approximately 100^{0} wind direction compared to the other wind directions and varied in the range of 0.015-0.085 for the 5 year period at these stations. This showed that the NO_x levels contributing to the peak seen in Fig. 2(a) at a wind direction of approximately 100^{0} has a very low chance of being detected at these stations. Even the high levels contributing to the wide peak seen at approximately 200^{0} in Fig. 2(d) at the Clinton station have only a 0.075 chance of being detected. As shown in Fig.7 these stations have even a smaller capability of detecting the peaks seen in Fig. 2 for other wind directions.

Even though the location of these stations with respect to sources may have been assigned through judgmental sampling, the results show that the capability of detecting the high emissions and especially when levels exceed maximum permissible values is very low. The chances of not detecting the high emissions from certain sources in the region are much higher. When high levels of NO_x are detected at a particular wind direction, then there is a high likelihood of similar levels existing at other wind directions too. Due to the lack of monitoring stations for detection at the other wind directions these high levels do not get detected. It is not unreasonable to extrapolate the percentage of higher NO_x levels detected at one particular wind direction to other wind directions as well in order to estimate the overall pollution from a particular source. For this purpose the polluting nature of a source (proportion of high NO_x levels) is assessed in a particular wind direction where it can be detected.

Proportion of high NOx levels at selected wind directions

At particular wind directions where higher mean levels were detected (Fig. 5), the proportion of levels above 6 pphm (twice the background level of 3 pphm) over a 5^0 range either side of the selected wind direction was determined. Fig. 8 shows these proportions at the selected wind directions.

Figure 8: Proportions of higher levels detected at selected wind directions. (a) Barney Point





(c) Targinie and Clinton



Fig. 8 shows that in most directions the proportion of higher emissions detected was less than 14% in the selected 10^0 wind direction interval. The proportion was found to be greater at 100^0 wind direction compared to the other wind directions at Barney point, South Gladstone and Targinie stations implying that the higher emissions were originating from sources located southeast of these stations. It is likely that similar proportions could be detected at other wind directions if there were stations aligned with these sources at those directions. Higher proportions were also observed at Barney point station for approximately 250^0 and 270^0 . This could be from one or more sources located west of this station. The frequency and wind speed from these directions is much less than at 100^0 (Fig. 6(a)) and may have reduced the proportion of higher emissions detected. It is possible that the sources located west of the Barney point station having a greater polluting capability than the sources located in the southeast.

Whenever maximum permissible levels (16 pphm) were exceeded for NO_x , it was mostly detected at the direction where a higher proportion of emissions were present. Fig. 9 shows the levels above 16 pphm and the prevailing wind direction at the time of detection.

Effect of wind on NO_x levels > 16 pphm

The effect of wind direction on high NO_x levels above 16 pphm is shown in Fig. 9(a)-(c).

Figure 9: Incidence of NOx > 16 pphm. (a) Barney Point



(b) South Gladstone





The incidence of NO_x exceeding 16 pphm appears to be always at wind directions where higher than normal mean levels were detected (Fig. 5). The detection at approximately 100^{0} at all stations are emissions from sources located southeast of these stations and is certainly wind assisted, since wind often prevails in these directions. The same applies to the high levels detected at Clinton in the $10-50^{0}$ interval which could be emissions from sources located northeast of this station (Fig. 1(a)). The high levels detected in the 250-350⁰ wind direction interval especially at Barney point and South Gladstone stations may have been detected at low wind speeds and low wind frequency, as a result the possibility of detection is low. These high emissions detected are most likely from sources located west of these stations (Fig. 1(a)) and could not be detected often due to the prevailing wind conditions dispersing the NO_x away from the monitoring stations. There may have been instances when NO_x emissions from these sources having exceeded the maximum permissible value and not been detected or reported. This would have posed a health risk to the population living close to these sources. The effect of wind speed on these high levels detected is shown in Fig. 10(a)-(c).

Figure 10: Incidence of NOx levels > 16 pphm (a) Barney Point



(b) South Gladstone



(c) Targinie and Clinton



The wind speeds associated with the measured NO_x levels above 16 pphm were less than 8 ms⁻¹ for most years except in 1998, when wind speeds up to 12 ms⁻¹ were associated with these high levels. This implied that it was possible to detect high NO_x levels over a wide range of wind speeds. Also NO_x levels above 16 pphm were detected at very low wind speeds less than 1 ms⁻¹ showing near perfect diffusion conditions. This indicated that the levels near the source may have been much higher than the levels actually detected.

The proportion of higher NO_x levels (>6 pphm) detected at different wind directions would provide some indication of the location of sources that are likely to produce emissions exceeding 16 pphm. This analysis shows that sources located southeast of Barney point and South Gladstone stations, west of Barney point station, northeast of Clinton station and southeast of Targinie station are most likely to emit high levels of NO_x. The chances of detecting this emission is less than 10% on most occasions due to the prevailing wind direction at the time of emission. The reason for having detected a larger number of high level emissions at Barney Point, South Gladstone and Targinie stations at approximately 100° is due to the prevailing wind at most times blowing from the southeast. As a result of this wind direction most of the NO_x emitted by the different sources will be spread across the region from the southeast to the northwest. Especially the emissions from sources located west of Barney point and northeast of Clinton are likely to have been carried in the northwesterly direction and not detected during the period for which this analysis was carried out. The inclusion of the station at Mt Milliner (Fig. 1(b)) in 2001 to monitor NO_x levels may provide more information on the northwesterly spread. There were also many instances when the prevailing wind was from the northwest which would have carried the NO_x emissions from the same sources as well as the sources located southeast of Barney point station in a southeasterly direction and not been detected. Based on the proportion of high emissions from these sources it is likely that in some instances the NO_x levels in the southeastern region may have exceeded the maximum permissible levels. The inability of the network to detect the spread of NO_x in the southeasterly direction was a significant shortcoming considering the popular residential development of Tannum sands being located in the southeast (Fig. 1(b)).

Although the spread of pollution depends on many factors such as surface topography, humidity, temperature, reactions in the atmosphere and wind conditions, it is the wind direction that had a major impact on dispersion and the ability of monitoring stations to detect these high levels. The analysis carried out for NO_x levels measured in this region can also be applied to other gaseous pollutants such

as SO₂, CO, organic gases and particulate pollutants such as PM10 to gain an understanding of the proportions that are detected. The network was able to provide exact NO_x levels at the monitoring site and its temporal variability, but not the spatial variability over the region especially from the southeast to northwest. This was the main limitation of the network. Monitoring authorities need to consider stating the wind direction along with each incidence when pollution levels exceeded maximum permissible levels. This will provide information on the most likely wind direction for detecting high levels of pollution. Using the information on the wind direction at which higher incidence of NO_x were detected and the proportion of high NO_x levels (>6 pphm) from a particular source, it will be possible to estimate the proportion of high NO_x levels at other wind directions due to the same source that may not have been detected. This will enable risk assessment to population groups located down wind from a source with no monitoring station. A way to overcome the problem of under estimating the occurrence of high pollution levels is to measure the emission from the sources for a length of time and use a validated inverse dispersion model to calculate source emission. This figure on source emission is then used to estimate the spread at different wind directions, which would give the required information on spatial variability.

This basic analysis carried out for this urban network of stations to identify the direction of spread of pollutants, capability of stations in the network to detect pollutants and the estimated proportion of high level pollution in certain wind directions that are monitored can be applied to assess limitations in other pollution monitoring urban networks. When the incidence of pollution levels exceeding maximum permissible levels is not assessed correctly, it will impact on the estimates of risk of population exposure as well as inadequate information will be passed on to authorities involved in environmental regulation and planning, which in turn may have an impact on future policy decisions.

Conclusion

Based on the analysis of NO_x measurements carried out at different wind directions it is shown that a higher incidence is detected at certain directions assisted by higher wind frequency, which resulted in higher mean levels measured in these wind directions. The overall capability of detecting NO_x in general varied from 1.0 - 8.5% in the selected wind directions that showed a higher incidence of NO_x being detected, compared to other wind directions. The proportion of higher NO_x levels (>6 pphm) detected at these selected wind directions varied from 0.5-14%. The analysis of wind frequency in the region showed that the extent of NO_x pollution may be greater than what is usually reported due to chances of non detection being high as a result of the prevailing wind carrying the pollutants away from the monitoring stations often in the northwesterly or southeasterly directions. This applies in particular to detection of emissions from sources located west of Barney point station and northeast of Clinton station, where there is no monitoring site aligned with the sources in the northwesterly or southeasterly directions. At certain wind directions although there was low incidence of NO_x detected, higher mean levels would have existed at other locations where there was no monitoring facility. Due to non detection in other wind directions the number of instances when maximum permissible levels may have been exceeded in the region would be much greater than what was actually detected and reported. A significant number of high levels were detected at the Barney point station when the wind direction was from the west, and at the Clinton station when the wind direction was from the northeast, where the capability of wind assisted detection was low as a result of low wind frequency in these directions. The proportion of high levels (> 6 pphm) of pollution from these sources responsible for the emissions was not different to others. In such situations higher levels of NO_x pollution from these sources may have existed at the more commonly prevailing wind directions, but not detected due to not having a monitoring station in line with the wind direction, being a limitation of the network to provide information on spatial distribution of NO_x in the region. Due to economic constraints it may not be possible to introduce more monitoring sites to gain a complete understanding of the spatial distribution of pollution in a region through measurements. This also limits the assessment of health risk to the population and damage to the environment.

The information provided by the monitoring network is limited to concentration levels at the monitoring sites and its temporal variation. Similar analysis can be carried out to assess limitations in other urban monitoring networks too. It is necessary to estimate the high emissions from sources under

certain wind conditions when the pollutants may be carried away from monitoring stations to populated regions totally undetected. Authorities responsible for monitoring and reporting need to consider estimating and reporting the extent of the undetected component of pollution from the different sources in the region using the results on detected pollutant levels and wind direction. When reporting the actual incidence of measured levels exceeding maximum permissible levels, there is a need to report the wind direction as well. This is in order to inform the public of the most frequent wind direction at which the high levels were detected and the capability of detection by the monitoring station at this wind direction. The health authorities and environmental policy makers need to be aware of the sensitivity and limitations of a monitoring network as well as to take into consideration the extent of the pollution that may be undetected when assessing the risk of population exposure and environmental damage. In order to gain a good understanding of the spatial distribution of pollutants in a region the source emissions will be required. For this purpose the levels at the point of emission needs to be measured, which could be difficult when tall plumes are involved. The more practical option is to determine source emissions using validated inverse dispersion models and measured levels at the monitoring sites. This will enable computation of spatial information by direct dispersion models, which could be integrated with the measured spatial information to overcome its limitations.

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BIOMASS - A POTENTIAL SOURCE OF RENEWABLE ENERGY FOR BRUNEI WITH LONG TERM EMPLOYMENT OPPORTUNITIES

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Abstract: The aim was to provide information on the biomass resources available in Brunei and possibilities of utilizing them for energy production, as well as deriving long term employment opportunities for the local population. There are different modes of energy production using biomass. Biomass is a source of renewable energy that is sustainable and environment friendly. There are many examples of successful energy production plants in developed countries using biomass. For Brunei use of municipal solid waste, agricultural residue and growth of energy crops are potential sources of biomass for energy generation. There is the possibility of using municipal effluent for irrigation of energy crops. Employment opportunities may arise in the areas related to agriculture (energy crop production, irrigation, research into crop yields) engineering (design, construction, operation and maintenance of processing plant) and transport (biomass to plant and distribution of end products). Economic benefits would be derived by the local community directly involved in biomass production and processing. Information of this nature will be of use to initiate feasibility studies on particular aspects of energy production and formulate energy policy in future economic development programs.

1. Introduction

At present the world's energy needs are mostly satisfied by petroleum crude oil, coal and natural gas. Their reserves are finite and being depleted rapidly. Biomass is the only natural renewable carbon resource large enough to substitute fossil fuels as an energy source. In scientific terminology all living matter is known as biomass. The energy stored in living matter is known as bioenergy. Biomass includes all water and land based living or dead organisms including non fossil based organic material such as wood from trees, harvested grasses, land and aquatic plants and their residue, animal waste, agricultural residue, sewage, organic components of industrial and municipal waste. The annual productivity of plants on land is estimated to be 130×10^9 tonnes and 100×10^9 tonnes in rivers, lakes and oceans (www.bioenergy.ornl.gov)

Plants use solar energy in photosynthesis to convert atmospheric CO_2 and water to carbohydrate, which is an organic compound. This is the key step in biomass energy production.

$CO_2 + H_2O + Chlorophyll light Carbohydrate + O_2$

The bioenergy is stored in the carbohydrate molecules. It is derived from biomass in a variety of ways using plants, industrial, commercial or urban wastes, agricultural and forestry residues such as coconut husk, rice husk and scrap wood. It can be in the form of solid, liquid or gaseous fuel, chemical products or converted to electric power.

Biomass has been the traditional source of energy for cooking and heating. In the mid nineteenth century biomass supplied over 90% of the energy needs for U.S. Bioenergy usage declined only after the introduction of fossil fuels (Klass 2004). For many countries in Africa, Asia and South America biomass still is a major source of energy supply, with India and China being the largest consumers of biomass energy (Klass 2004). Over 50% of the world's population use wood, dung and plant residue for cooking which generates over 300 GW of power (Twidell and Weir 1986)

Burning of biomass produces heat, which is used to boil water and generate steam that turns turbines and produce electricity. Biomass is also heated to convert it to a gas and drive a turbine. The waste heat from the gas turbine is used to drive a steam turbine, converting more of the biomass energy to electricity. Biomass is blended with coal in coal fired systems to generate electricity by co-firing.

Biomass is a renewable energy source, it releases CO_2 emitted during conversion to energy that has been absorbed from the atmosphere by plants during the growth phase. Therefore biomass as a fuel is considered to be carbon neutral since there is no increase in CO_2 levels in the atmosphere. Even after allowing for emissions of CO_2 during planting, harvesting, processing and transportation of the biomass, the replacement of fossil fuel with biomass energy is expected to reduce net CO_2 emissions by over 90%. Also biomass is a carbon fuel that can be transported, stored and processed into a range of fuel products such as wood chip, pellets, biodiesel, biogas, methanol, ethanol etc. There is also the potential to produce hydrogen for fuel cells and Jet Fuel.

Generation of biomass energy does not imply cutting down trees or tropical rainforest, it is about making better use of available biomass resources and planting new forests and energy crops to provide real sustainable sources of renewable carbon fuel. It addresses the main issues of concern such as sustainable development, environmental protection, renewal of natural resources, social equity and long term economic growth.

This article gives a brief description of the biomass resources available, different techniques of energy production using biomass and economic benefits that are being derived. The present resources that are available in Brunei for biomass energy production and the employment opportunities that would result from production and utilization of biomass energy have been discussed. Information of this nature will be useful for initiation feasibility studies to formulate energy policy related to future economic and regional development.

2. Biomass Terminology

Biopower is the power generated using biomass feedstock.

Biorefinery is a processing plant for converting waste biomass feedstock to fuels, energy and other products.

Biofuel is solid, liquid or gaseous fuel produced from biomass.

Biogas is a medium energy content gaseous fuel also known as natural gas and produced from biomass by methane fermentation.

Bioenergy crops are fast growing crops used as biomass for energy production.

Biomass residues are agricultural, forestry residues and animal waste.

3. Biomass Resource

The earth's biomass resource exists in a thin surface layer called the Biosphere. Although this is a small fraction of the earth's surface, it is an enormous source of energy that is replenished continuously on land, in rivers, lakes and oceans. It has a capacity 100 times that of world's annual energy consumption. The largest component is forest biomass, which amounts to 80-90% of the total (Klass, 2004). The next is marine biomass in terms of net annual production, which has a long turn over time in the marine environment. The biomass resource is the fourth largest after coal, oil and natural gas and the only renewable carbon resource large enough to be used as a substitute for fossil fuels. Currently it is used for heating (wood furnaces, stoves in homes and bioprocess industries), cooking (in developing countries), transportation (manufacture of fuels and ethanol) and increasingly for electric power

production. At present about 2% of the land based production is being converted to biomass energy world wide generating 35 GW of power. In the U.S. 7 GW of power is generated using forest product industries and agricultural residues, 2.5 GW using municipal waste and 0.5 GW using land fill gas (<u>www.bioenergy.ornl.gov</u>). Many developing countries meet over 70% of their energy demands using biomass, mainly through burning for cooking and domestic heating. Some industrialised countries such as Sweden (17.5%), Finland (20.4%) and Brazil (23.4%) meet a significant portion of their energy demands from biomass processes other than direct burning (Klass 2004).

Biomass could produce energy on demand (unlike solar and wind energy where the resource is not available at all times). The burning of biomass does not produce extra CO_2 since it releases what has been absorbed at the time of photosynthesis. There is low level release of NO and NO_2 due to burning and additional greenhouse gas emissions due to use of farm equipment and inorganic fertilizers on biomass crops. There is no extra heat produced during burning since the slow decay if allowed to occur will generate the same heat over a longer time span. If consumption rate does not exceed the natural renewal rate then there is no disturbance to the biochemical cycle.

Therefore biomass resources are renewable and sustainable if well managed. Present biomass technologies are efficient and clean. Burning biomass instead of fossil fuels can reduce emissions of the gases responsible for acid rain as well as CO_2 emissions, being the main gas responsible for global climate change. Biomass agriculture and forestry holds great economic potential especially for countries in the tropical and subtropical regions. Development of this potential by developing countries would enable them to derive economic benefits (Smith, 1985).

4. Biomass Energy Production

The floor chart described in Fig. 1.1 shows the modes of biomass production and different conversion processes for producing biopower, biogas and biofuels.

Figure 1.1: Sources of biomass and different conversion processes (Smith 1981).



4.1 Solid Mass Fuel

This is the chemical energy extracted from wood and green plants through burning. Cow manure and grass also burn, but generate a lot of smoke. A wide range of biomass feedstock can be processed into solid biomass fuels such as chips and pellets. This can replace fossil fuels in domestic, commercial and industrial boilers to supply space heating, process heating or steam for a turbine.

4.2 Ethanol (C₂H₅OH)

This is a liquid fuel produced from biomass by fermentation of sugar under acidic conditions. Sugar is extracted from biomass feedstock such as sugar cane, sugar beet by crushing and washing and from grain, cassava and cellulose by hydrolysis. The sugar syrup is mixed with yeast and kept warm in a tank known as a digester, for the yeast to break down the sugar to ethanol. In practice about 47% of the fermented sugar is converted to ethanol. Then by distillation ethanol is concentrated and by dehydration pure ethanol is produced. This process requires heat which is supplied by combustion of other biomass. The ethanol is combined with gasoline as fuel in cars and trucks. Ethanol delivers more power than gasoline.

Advances in biotechnology may allow production of ethanol from many biomass feedstock, energy crops, agricultural and forestry residues, municipal waste that contain cellulose, which can be broken down into sugars for fermentation (Biofuels, DOE/GO-102001-1434, Sept 2001).

4.3 Biogas

This is a mixture of CO_2 and methane. It is produced using plant material and animal waste by microorganism in the absence of O_2 (anerobic) or air through bacterial action in a sealed tank known as a digester. The methogenic bacteria over a period of between 10 and 25 days, through an anaerobic

digestion process converts 40 to 60% of the dry mass of a liquid biomass feedstock in the mixture to biogas in the form of bubbles which collect at the top of the tank. The bacterial action is sensitive to temperature, acidity and amount of water. There are 3 temperature ranges 20° C, 35° C and 55° C which favor different types of bacteria. Digestion at higher temperature proceeds more rapidly than at lower temperatures with gas yield doubling at every 5° C increase in temperature. For successful operation constant temperature conditions and suitable input material has to be maintained. When the production rate slows down the mixture is replaced and the process is recommenced. The balance of the feedstock is recovered as a stable residue rich in nitrogen, which may be separated into liquid and solid fertilizer. This anaerobic digestion process recycles municipal waste, algae, water weeds, animal slurries and food waste into safe organic fertilizers while generating renewable energy. Pig barns and sewer pipes are large scale sources of biogas. For small scale processes 3-4 m³ vessels are used in rural regions of India and China. The extracted gas has been used to heat and light homes and fuel buses. The economic benefits are high when the digester is placed in the general flow of waste material that is already present, such as sewage systems, piggery washings, cattle shed slurries, abattoir wastes, food processing residues and municipal land fill dumps. In these situations there is no need for collection of material.

Biogas generation is particularly attractive to integrated farming where the full ecological cycle can be emulated in a single farm. This requires integrated design, good construction standards and regular maintenance.

4.4 Biomass Gasification

Biomass is heated to temperatures of the order of 800 to 900° C without O₂ it gasifies to a mixture of CO and H₂ known as syngas. This gas mixes more readily with O₂ and burns more efficiently and cleaner than solid biomass. It improves the efficiency of large scale biomass power generating facilities.

There are a wide variety of gasification reactor concepts available, including updraft, downdraft and fluidised bed designs. The gas is cleaned to remove tars and other contaminants, such as particulates and alkali metals. Syngas can be used directly in a furnace, in a gas engine or turbine or can be further refined for use in fuel cells for transport. It mixes easily with chemical catalysts and can be convered into useful chemicals and materials.

4.5 Pyrolysis

Solid biomass such as wood, crop residue, municipal waste and coal can be liquefied by heating to moderate temperatures (550 0 C) without O₂. This process is known as pyrolysis and has been practiced for a long time on wood, converting it to charcoal with double the energy density. Fast pyrolysis is a thermal decomposition process that occurs at moderate temperatures with a high heat transfer rate to the biomass particles. This liquid can be used directly as fuel, as well as for high-value chemicals and materials.

Several reactor configurations have been shown to achieve yields of liquid product as high as 75% based on the starting dry biomass weight. They include bubbling fluid beds, circulating and transported beds, cyclonic reactors, and ablative reactors.

The liquid also known as pyrolysis oil or bio-oil can be readily stored and transported. It has been successfully tested in engines, turbines and boilers. Also has been upgraded to high quality hydrocarbon fuels at a high cost.

4.6 Biodiesel

This is produced from vegetable oil extracted by crushing oil seeds. Waste cooking oil and animal fats can also be used for the purpose. The oil is strained and estrified by combining with methyl alcohol under alkaline conditions. The resulting methyl ester is separated from the co-product glycerol and isolated as biodiesel. It is slightly less efficient than petroleum diesel and is free of sulpher.

Biodiesel from agricultural crops such as soya bean and canola have the potential for making significant contributions towards achieving energy security. It may have to compete for land use with agricultural production of food and fibre as well as industrial uses. Therefore these crops do not show

economic viability at present. Use of recovered cooking oils and other materials currently show greater promise of economic production of a diesel fuel substitute (Zhang et al 2003).

4.7 Land fill Gas

Methane is extracted from the organic component of municipal waste used in land fills.

Decomposition of the organic matter in the waste produces methane and carbon dioxide, which are the principal components of landfill gas. The composition of the gas is controlled by products of microbial reactions in the landfill. In general, a landfill will go through three different stages with different bacterial types predominating in each stage.

Solid waste initially decomposes aerobically producing carbon dioxide. As the oxygen is used up, anaerobic microorganisms predominate. These bacteria continue to produce carbon dioxide, but the process proceeds into second-stage anaerobic decomposition, where both methane and carbon dioxide are produced at approximately equal proportions. The gas is recovered by inserting a system of interlinked vented pipes into the landfill and used in gas turbines. The rate of gas production depends on the volume, composition, age, temperature and moisture content of the waste,

4.8 Biomass Crops

Switch grass, willow, poplar, sorghum, alfalfa and corn are some crops specially grown on unused lands for biomass energy production. Road side land is also considered suitable since the crops could absorb CO₂. Biomass crops improve water quality by providing continuous soil cover to stabilize soil erosion and help build organic matter in the soil. The crops do not require extensive fertilization, therefore lower levels of nutrients get transported as run off from production sites. Most biomass crops are perennial so that they are grown over a 5-15 year period with the development of extensive rooting systems for below ground carbon storage. Below ground carbon and organic matter improves soil quality and nutrient reserves. Biomass crops require only 1/10th the amount of herbicides and pesticides on average compared to agricultural crops. Biomass tree crops store the carbon in stems and branches till harvested for energy production.

Short rotation biomass crops can be grown using municipal effluent for irrigation. Wastewater from homes, businesses and industries carries 98% water and 2% dissolved or suspended solids. Usually the effluent is rich in nutrients, biochemicals and microbials. Municipal effluents are being used for crop irrigation after partial treatment (Sharma 2005).

5. Economic Benefits from Development of Biomass Energy

Development of biomass energy supply creates new employment opportunities in agriculture such as growing energy crops, in engineering such as construction of processing plants, operation and servicing of plant, supply of plant components, in transport such as delivery of biomass to processing plant and distribution of end products. As coal fired plants become less favorable, biomass fuel production offers potential re-employment to people made redundant in the coal industry. When locally produced biomass supplies local energy markets, it keeps the revenue for investment in local rural economies. Whereas money spent on fossil fuels is of no use to local rural economies since the revenue benefits remote multinational companies and their shareholders.

The need to grow biomass crops will bring unused lands into production, improve wildlife habitats, help conserve and promote biodiversity as well as enhance the rural environment. The use of the organic material from urban waste as biomass reduces the need for landfill sites as well as lowers the emission of methane, a green house gas to the atmosphere.

Biofuel production from biomass is likely to be economic only if there is a ready supply of concentrated material close to the production site such as waste from animal enclosure, off cuts and trimmings from saw mills, municipal sewage and agricultural residue, so that it minimizes transport and handling costs. Utilization of the biofuel at site leads to further reduction in power generation costs. The presence of moisture in biomass often leads to significant loss in useful thermal output.

Currently there is capacity to provide 7 GW of power using biomass from more than 350 plants in the U.S. By 2020 the aim is to provide 30 GW of biomass power and to meet 60% of the fuel needs from 10 million acres of energy crops and biomass residue. This process is expected to provide employment for 150,000 and revitalize rural economies (Biopower Program Activities Overview).

In Brazil there are over 500 fermentation and distillation plants in operation processing crops grown throughout the year producing over 16 billion liters of ethanol and providing employment for over half a million people. Using 0.3per cent of the land area in Brazil it is expected to supply all the petrol needs for the country (Smith 1981). Australia, France, Sweden and USA are also embarking on biological ethanol production using surplus agricultural production and forestry wastes. In USA at the beginning of 2005, 81 ethanol plants in 20 states had the capacity to produce nearly 4.4 billion gallons annually and an additional 16 plants are under construction for a further 750 million gallons of increase in capacity (www.eere.eng.gov).

In India, China, Taiwan and Korea there are many thousands of family sized biogas units in operation in rural areas using animal and agricultural waste. The biogas generated from these units is used for operating farm machinery, lighting, cooking, heating etc. In Europe there are many facilities converting municipal solid waste into heat for electricity generation with links to the local grid. In U.K. methane gas is produced from sewage is compressed and mixed with diesel to power vehicles. Denmark has few thousand straw furnaces producing heat for power generation (Lewis 1983).

6. Biomass Energy Potential in Brunei

Present power generation in Brunei is fossil fuel based using local resources. The economy of Brunei depends heavily on the local fossil fuel reserves as the main source of energy supply and export income. The demand for energy locally is expected to rise with population growth and industrialization. Therefore an urgent need exists for alternate sources of energy for domestic and industrial use in the future in order to reduce the rate of depletion of the fossil fuel reserves, which are vital to sustain the economy as a source of export income in the future.

Due to frequent cloud cover over Brunei, solar energy is not very promising as an alternate source for power generation, but may be more suitable for water heating. Biomass energy may be a suitable option due to the present availability of municipal waste for gasification, biogas production and incineration for steam generation, waste vegetable cooking oils for biodiesel manufacture, open spaces between forested regions for growing energy crops, use of municipal effluent for irrigation of energy crops, agricultural residue and poultry manure for biogas generation etc.

6.1 Use of municipal solid waste

Brunei being a high income consumer society, a large amount of municipal solid waste is generated, which is currently being used as land fill for housing projects. The waste could be incinerated, gasified or used for biogas generation. Gasification has produced electricity with an efficiency of 34% (Murphy et al 2004). Biogas could be generated by digesting the organic fraction and converted to transport fuels. Incineration of the non recyclable, non organic component has produced electricity with 20% efficiency and has a thermal efficiency of 55% (Murphy et al 2004). The organic fraction of this waste has also the potential for generation of large quantities of methane (land fill gas), which can be collected by insertion of pipes with perforations into the waste matter and used to operate a gas turbine.

In Malaysia calorific value of the solid waste was in the 1500-2600 kcal/kg and the amount of solid waste generated is 1.7 kg/person/day. The potential of an incineration plant with a calorific value of 2200 kcal/kg was found to be is 640 kW/day (Kathirvale 2003). It is very likely that the biomass content of municipal solid waste in Brunei is similar to that in Malaysia, therefore the calorific value per kilogram of waste could be the same. This enables determination of the power generating potential based on the amount of waste collected.

6.2 Biomass crops

Sustainable harvesting of crops is expected to supply 7% of world's energy demand in the future. In Brunei there are many open spaces between densely forested regions, which can be used for cultivation of biomass crops such as cassava and sugar cane primarily for ethanol production on site. Coconut oil, palm oil and soya bean oil could be produced and used as biodiesel (waste cooking oil from restaurants included). Tropical conditions in Brunei are ideally suited for year long cultivation of these crops.

Growing biomass crops improves the biodiversity of the environment and will be an additional attraction for promoting eco-tourism. With advancement in technology, development costs will reduce and the end product will become more competitive with price of fossil fuel. The ethanol produced from corn selling at U.S.\$1.20-1.50 per gallon contributes to 1% of U.S. national gasoline consumption (www.bioenergy.ornl.gov). In 2001 more than 20 million gallons of biodiesel was sold in the U.S (Biofuels, DOE/GO-102001-1434, Sept 2001). Biodiesel made from rape seed is used in Germany, France and Italy. An increase in demand for biodiesel can be met by supplies of the essential methyl ester from the detergent and fatty acid industries.

Partially treated municipal effluent could be used to irrigate the energy crops. In California 27 GL per year of municipal effluents are being used to irrigate vegetable crops (Sharma et al 2005).

6.3 Biogas from agricultural residue and poultry manure

In rural areas of Brunei many families cultivate rice, bananas, coconuts, vegetables and raise poultry. The vegetable and banana plant residue after harvest, coconut and rice husk as well as the poultry manure could be used to operate family sized or community based biogas units similar to the Gobar units in India (Lewis 1983). These units could provide biogas for cooking, water heating, lighting and even generating electricity to the local grid. In Brunei there are sago palms grown commercially for extraction of carbohydrate from the trunk. The remainder of the palm can also be used as biomass in these units. Also the by products from these units are useful as fertilizer, soil conditioner or animal feed to fish or duck ponds.

6.4 Establishment of modular systems

Modular biomass energy generation systems in the 5kW to 5 MW (www.eren.doe.gov) can be established in rural regions of Temburong, Tutong and Belait where there is no electricity supply. Using locally available biomass such as wood, crop waste, animal manure and landfill gas, power could be generated for lighting, refrigeration and other domestic uses. Some systems are portable and can be moved close to local biomass crops and agricultural residues to overcome the need for transportation of biomass over long distances.

The modular systems consist of a fuel processor and an electricity generator as well as can be connected to the customer's side of the power grid to supply unused power to the grid, which has been found to be economically attractive. If this is feasible in the long term it would reduce the consumption of fossil fuel for power generation. These systems have been found to be simple to operate and required no special skills. Prototype modular systems have been demonstrated in a Philippine village in 2002 and have the potential to supply electricity to 2.5 million people (www.eren.doe.gov).

6.5 Electricity through cogeneration from biomass

Electricity generation in Brunei is by using fossil fuels. Using biomass for cogeneration enables reduction in the use of fossil fuel. This is a major saving in the current climate of high fossil fuel prices and helps extend their period of use. This process is economically viable only if the increased cost of installing, maintaining and operating the cogeneration facility is less than the savings on fossil fuel.

6.6 Source of economic benefits and employment opportunities

Development of a biomass industry in Brunei would bring economic benefits through manufacture of new products using local raw material leading to job creation, opening new markets for rural industrial output, reduce migration to urban areas as well as research and development of biomass related technology and greater energy security in the long term. Biomass can encourage farmers to grow new cash crops as an additional source of revenue. Also use crop residue as a biomass resource reducing disposal costs and provide an additional source of income. The use of biomass energy crops for power production opens a whole new market for agriculture creating employment in producing, processing, distribution and in service industries such as plant manufacture, maintenance and supply of components. Most of the employment is created in the local region and the income is retained by the local community. On average an ethanol plant in the US provides 41 full time jobs (www.eren.doe.gov).

Using biomass, products such as organic acids, glycerine, cellulose polymers, foams, lubricants and inks can also be manufactured, which are currently derived from petroleum by products.

Most biomass production and utilization will occur in rural areas. The biomass may have to be grown, collected, dried and burnt or fermented. This requires resources, infrastructure and expertise. Therefore the rural population may require initial financial and technical support to set up and maintain these biomass energy units. A sustainable biomass industry once set up could employ graduates in science and technology to provide training and advice to rural regions on energy crop production and processing of biomass, as well as initiate research and development of techniques suitable to local biomass products and conditions. Higher education institutions in Brunei need to consider including courses in renewable energy especially in biomass energy to train staff who could initiate and develop a biomass industry in the future.

The regional impact of biomass energy in the southeast of U.S. has been the generation of 71,000 jobs and \$1 billion of annual income. In 2001 consumption of biomass energy in the U.S. was equal to 17.6% of total energy imports (Klass 2004). In Thailand biomass energy consumption has increased 68% and in the next 8 years the power generation plan is to produce 1055 MW from biomass and 28.8 MW from Biogas (Prasertsan and Sajjakulnukit 2006). This gives an indication of the economic impact biomass energy is going to have in the current climate of high fossil fuel prices.

6.7 Policy recommendations

A government policy initiative is needed to emphasize and promote the production and utillisation of biomass energy. This policy may have to be supported by a legal and financial framework to provide subsidies to initiate biomass energy production. Government agencies concerned with energy, environment, agriculture, industry and finance may have to coordinate their effort to provide strong infrastructure for the biomass energy initiatives. Technical standards for biomass energy systems and equipment may have to be established to guide equipment manufacturers and importers.

Human resources may have to be planned and developed to create awareness, disseminate information to promote and sustain biomass energy applications in the local communities. Successful applications of biomass energy may have to be demonstrated to give the local community especially the private sector confidence in biomass energy. A database on biomass energy may have to be developed to help energy planners, manufacturers and users.

7. Conclusion

There are different sources of biomass and several methods of producing energy and related products. Energy production from biomass in different countries has been found to be economically viable. There are several sources of biomass for energy generation presently available in rural areas of Brunei with possible long term sustainable direct economic benefits and employment opportunities to the rural community. Municipal solid waste is a ready source of biomass available in urban areas for gasification or cogeneration of electricity. There is municipal effluent available for irrigation of energy crops grown on waste urban lands. Financial and technical support may be required particularly for the population living in rural areas to initiate use of biomass for energy generation. To provide the required technical support personnel may have to be trained at the various institutions of higher education on the different aspects of energy generation using biomass. Fundamental information of this nature will be useful to formulate future renewable energy policy and initiate feasibility studies in particular aspects of energy production using biomass.

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ABSTRACTS OF FOS PUBLIC LECTURES 2005-06

AUTONOMOUS ROBOTS FOR LAND, WATER AND AIR

Frank Nickols

Department of Mechanical Engineering Dhofar University, Salalah, Sultanate of Oman.

The Faculty of Science organized a public talk on 25 January 2006 at 4 pm in room FSM 2.18 by Dr. Frank Nickols. Dr Frank Nickols was a visiting speaker from the university in the sultanate of Oman. The title of the talk was "Autonomous Robots for Land, Water and Air"

The talk showed numerous movie clips concerning the robots that Dr. Nickols and his students have designed and built in Singapore and Hong Kong. There was a short presentation concerning robot inverse kinematics, behavior patterns, and embedded parallel processing using microcomputers. Mathematical concept was kept to a minimum while the movie clips, photographs and lively discussion was kept to a maximum in the talk. More then 60 people mainly from UBD and ITB attended the talk.

Some of Dr Nickol's robots (from www.franknickolsrobots.com/robot.htm):

Axi-Symmetric Omni-Bot: Omni-directional" means that the robot can walk in all directions including rotating whilst translating like in a Viennese waltz. Furthermore, the body possesses 6 degrees of freedom i.e. the body can rotate and translate (albeit limited) about and along its fore-and-aft axis, its athwartships axis and its vertical axis. This means that the body of the robot can be a stabilised platform.



Spider Robot: One of the more developed of the walking robots is this 8 legged spider robot. (Remember spider=8legs, beetle=insect=6 legs). Each leg is actuated by 3 servos (Futaba S3003 and S9450) which makes 24 servos total. Because the robot has 3dof legs then it is capable of being omnidirectional.



Beetle Robot: This beetle robot has 6 legs with 2 servos controlling each leg. The robot can move forwards, backward and turn to the right and left at many different speeds. The robot can be controlled using a radio remote controller or in autonomous mode, it moves under its own intelligence by detecting obstacles with a pair of 'whiskers'.



Cuttlefish Robot: This robot was designed to emulate the fin motion of a cuttlefish. The 'fins' are connected to 12 servos on each side. The servos move in a sinusoidal motion to create a propulsive force. The robot sits on the surface of the water with the fins below the waterline.



TRANSCRIPTS OF FOS PUBLIC LECTURES 2005

RECENT ADVANCES IN MATERIALS FOR WEALTH AND HEALTH

P. Hing

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Abstract: This paper stems from a public lecture given on 3rd February, 2005 in the Physics Department, Faculty of Science, University of Brunei, Darussalam. The presentation reviews recent advances in some materials related to the microelectronics and life sciences with bearing on wealth creation and enhancing the quality of life. In particular advances in nano materials and processes that have led to the development of highly sophisticated and powerful microelectronic integrated devices for computers, business machines, data storage and retrieval systems, health monitoring, drug delivery, medical imaging and tissue engineering will be presented and discussed.

1. Introduction

Few would dispute that throughout the ages the well being of a country and its citizens have always been closely linked with the ingenuity with which materials have been exploited to meet societal needs.

And this is not any different today. Except that today most of the materials we use in our daily life are also very much more complex and sophisticated. Most people are not very aware of this. I hope to show how continuing advances in materials is fuelling not only the engine of growth and in the process creating wealth, but also enhancing the quality of life. Immense strides have been made in materials for better health monitoring devices, for body repair and drug delivery system and so on.

High on my list of materials that are fuelling the engine of growth and creating wealth are microelectronic materials and biomaterials. This does not imply that advances in structural materials such as advanced ceramics, engineering polymers, functional ceramic and polymer composites are not making useful contributions.

Materials play a very pivotal role in our daily life. They are needed in practically every sphere of human activity – be it for

- □ Microelectronics and electronics industries
- □ Land and sea transportation
- □ Aerospace & space exploration
- Communication and information
- □ Sports and recreation
- □ Energy
- □ Advancement of medicine
- □ Business and commerce
- \Box Defense
- □ Lighting
- □ Agriculture
- □ *Housing & infrastructure development*
- □ Environment monitoring and protection

In this review, I will confine the discussion primarily on materials for the microelectronic and electronic industries and those that are relevant in health monitoring, drug deliver, body implants, medical imaging and tissue engineering.

2. Invention of the Transistors

Figure 1: First point contact transistor constructed with Ge single crystal on 16 December, 1947 by Bardeen, Shockley and Brittain at Bell's Lab.



Fig. 2: Inventors of the Transistors



It is very appropriate to mention at this stage the pioneers of the transistors. In Figure 2, we can see William Shockley (sitting); standing on the left is John Bardeen; and on the right is Walter Brattain. These three researchers from Bell Laboratory in the States won the Nobel Prize for physics in 1956 for their invention of the transistor, which was the first point contact transistor made from a germanium single crystal in 1948. A picture of the original transistor is shown above the inventors.

These researchers had a mission, namely, to make the vacuum triode valve invented in 1906 redundant. Their invention required a million times less energy to perform similar switching and amplification operation than the vacuum triode valve!!

The vacuum triode tube was invented by Lee de Forest around 1905, and extensively used as a switch and amplifier. It was the workhorse used to control the current electronically, thus replacing the manual switch. This dominated the electronic industry until 1950 or so when the transistor started to take over.

3. Trillion Dollar Electronic Industries

The discovery of the transistor has enabled today the creation a trillion dollar electronic industries. This will be illustrated later on. There is no indication at present that the microelectronic and electronic industries are showing any sign of slowing down. In the microelectronic industries, silicon semiconductor has long superseded the germanium semiconductor because of smaller leakage current in silicon devices, and also better performance at higher temperature. Silicon semiconductor still reigns supreme, although other compound semiconductors from III-V are making some inroads.

Presently electronic grade silicon is used to grow large single crystal up to 12 inches in diameter. The silicon ingot is sliced into thin wafers and polished down to sub-nanometre surface finish by a combination of chemical and mechanical polishing (CMP) for the production of very complex integrated circuits.

These wafers are then subjected to a very large number of deposition processes and can take several weeks before being taken out for dicing and connection to external circuits and packaging. The cost of building a wafer plant runs into several billion dollars.

The silicon chip in the form of very large scale (VLSI) integrated circuits is used in computers and in all types of electronic appliances.

How can such inventions in the space of less than 50 years or so completely revolutionize the way we work and live today? This is truly the miracle of science and engineering at work.

Materials scientists have made tremendous contribution to understanding the behaviour of materials and Materials engineers, on the other hand, have contributed in no small measure in designing and developing extremely clever processes for producing extremely complex, highly reliable and cost effective microelectronic devices for the electronic industries.

In this review, I will confine the discussion primarily on materials for the microelectronic and electronic industries and those that are more relevant in health monitoring, drug deliver, body implants and tissue engineering.



Figure 3: Production of the IC chip

Mass production of IC chips by planar technology leads to miniaturized, extremely reliable and cost efficient integrated circuits. The flat edges on the wafers identify the crystal orientations for the fabrication process. From S O Kasap – Principles of Electrical Engineering Materials and Devices.

Figure 4 shows a schematic of the Field Effect Transistor (FET) and Figure 5 shows one type of FET known as Metal Oxide Semiconductor Field Effect Transistor (MOSFET). Because both n and p channels are formed

It is of interest to note that specially doped silicon semiconductors together with a range of other materials are needed for the fabrication of a reliable (MOSFET) transistor, and other type of transistors.

Figure 4: Cross sectional area of a p-type channel MOSFET



Figure 4 shows a cross sectional area of a p-type channel MOSFET (Metal – Oxide – Semiconductor Field Effect Transistor). The device is produced by integrated –circuit (IC) fabrication technology. The MOSFET has been described as the workshop of modern electronics industry. Various types of MOSFET transistors such as PMOS and NMOS are available; most common being the CMOS (Complimentary MOS consisting of a PMOS and an MOS side by side). This is shown in Figure 5.

Figure 5: A Complimentary MOSFET (abbreviated as CMOS) transistor. It consists of a PMOS (p-channel) and an NMOS (n-channel) Field Effect Transistor. Note the range of materials needed to construct such a sophisticated and reliable transistor.



Figure 6: The cross section of a Bipolar npn Transistor. Two types of charge carriers are involved, electrons and holes, hence the term bipolar.



Figure 7: Bipolar transistors showing the various materials used.



4. Nanotechnology

The Pentium IV microprocessor, with the latest technologies contain some 42 million transistors of 60 nm gate length with oxide thickness of 1.5 nm. $1 \text{nm} = 1 \times 10^{-9}$ metre. The human hair is about 1000 nm in diameter. See Figure 8 below.

Figure 8: Moore's law. Gordon Moore (right side, cofounder of INTEL) in 1956 predicted that the feature size for the memory chip for <u>Dynamic Random Access Memory</u> (DRAM) and the microprocessor chips (MPU) should get smaller and smaller every year or couple of years. The trend appears to be possible in the years ahead only with new advances in materials and materials engineering.



Figure 9: Pentium IV and Itanium² chips. These chips are the workhorse in most of the computers today.



Pentium IV chip - 42 million transistors



Itanium² Chip – world most powerful chip capable of performing hundreds of millions of operations per second.

5. Heat Management of Microelectronic Devices

The number of transistors on a chip is also limited by the power dissipation of the chip. This is shown in the Figure 10. In order to enable more powerful and faster personal and portable computers to be developed, there is an urgent need for more efficient design and innovative use of heat sinks with highly thermally conductive materials.

Heat management requires the development of novel and highly thermally conductive materials or processes for new generation of computers. Figure 11 shows the thermal conductivity of some heat sink materials. High on the list is diamond which has a thermal conductivity of pure single crystal is of the order of 2000 W/mK.

Figure 10: Predicted power density of INTEL MPU'S.



Figure 10 shows the predicted power density of INTEL MPU'S if Moore's scaling laws are continued. This is why your computer/laptop gets very hot. Hence there is an urgent need to manage the heat generated, despite ventilation system of pushing the hot air built up inside the lap top out every now and then. Heat Management is an important issue being addressed. Materials play an important part in heat management.

Figure 11: Materials for Heat Management of advanced microelectronic devices.

Diamond has unmatched thermal conductivity

Thermal Conductivity of Typical Thermal Management Materials



There is a need to develop economical processes for the fabrication of high thermal conductivity materials such as diamond, aluminium nitride, silicon carbide for the next generation of advanced microelectronic devices.

AlN is an interesting material. It is electrically insulating and yet with relatively high thermal conductivity if we can remove all the oxygen in it. Unfortunately even a small amount of oxygen at ppm level reduces drastically the thermal conductivity due to phonon scattering.

Thus the processing of both polycrystalline and single crystal aluminium nitride presents a challenging processing problem for scientists and materials engineers. It is of interest to emphasize that materials science and engineering will continue to play an even greater role in the development of the next generation of nanoelectronic devices.

Another key issue that could limit the development of microelectronics in the future is the high cost of setting up a complete microelectronic system. As illustrated in Figure 11. As the cost escalates, there may be difficulties in continuing to decrease the cost per function by 20 - 30% every year in the future.

6. Issue of Manufacturing Cost



Figure 11: Cost for setting up systems for manufacturing been increasing.

It can be seen that the global market per annum today for electronic devices, and systems amount to over a trillion dollar per annum (about 20% of world economy). Semiconductor market alone is estimated to be over 100 B US\$. This is really a colossal industry based primarily on the a few selected materials, but the key material is still based primarily on silicon.

7. Wide Range of Materials Besides Silicon Semiconductors for Devices

SiiGe alloys are being developed for the new generation of advanced microelectronics because of its higher electron mobility. Other compounds of silicon such as metal silicides (basically ceramic based materials) with very low resistivity are increasingly being used as electrical connectors in advanced microelectronic devices to eliminate electromigration. Metal silicides such as iron silicide are attracting a lot of interest as light emitting materials, with potential in the development of integrated optoelectronic devices.

Another material of great significance in the microelectronic industries is silicon dioxide, SiO_2 , a component of glass. Without it there is no microelectronic industries we have today. This is because it is an almost perfect insulator with a low dielectric constant of around 3. Research on both low and high dielectric constant material is subject of intensive research.

Figure 12: Hard disc drive requires a lot of advanced materials and microelectronics.



Great strides are being made in the development of porous silicon for light emission, transistors for biochips, and devices for self health monitoring, lighting applications, compressors for refrigerators, flat panel displays, glass fibres for polymer composite reinforcement, fibre optics, special chemicals for ceramic and electronic industries.

8. Materials with Large Band Gap

I would like to mention briefly recent development in large band gap materials, in particular on nitride based ceramic materials such as such AlN, InN, GaN ... Metal nitrides are basically ceramics if we consider the broad definition of ceramics, namely, a material consisting basically of a metal and a non-metal such as oxygen, nitrogen, carbon, silicon, boron, phosphorous ...

AlN, InN and GaN and their alloys are all direct band gap semiconductors which crystallize in the wurtzite (hexagonal) structure. The interesting features of these materials are their ability to emit light covering the whole of the visible spectrum, including uv. Some of these nitrides such as AlN has a band gap of 6.2, GaN 3.2 eV, and InN 1.9 eV. InN has been reported to have a band gap of less than n 1 eV with large built up of negative charges on the surface making it suitable to fabricate hybrid devices made of metals and semiconductors. AlN and GaN are stable chemically. The n and p doping of GaN has been achieved with silicon and magnesium respectively. Doped GaN semiconductors have large saturation drift velocity compared with other III-V and Si semiconductors. Thus semiconductors based on the nitrides are suitable for many novel electronic and opto - electronic applications.

Key applications are in

1. Green, blue (in production) and uv (in development) light emitting diode (LEDS), for displays and health monitoring.

2. Blue/uv laser diodes such as vertical light emitting laser diodes for data storage (HD- DVD), printers, and medical diagnostics.

3. White light sources of high-efficiency low cost replacement for incandescent and fluorescent lighting thus reducing electricity consumption and reduced mercury contamination.

4. High power (rf) Field Effect Transistors (FETS) to replace silicon devices at low frequencies (1-3 GHz for mobile phone base amplifiers) and travelling wave tubes at X-band and above (radar)

5. High temperature electronics and sensors, including uv detectors

6. All optical switches, lasers, and semiconductor optical amplifiers (SOAS) operating at 1.55 mm based on inter sub band transitions

7. Potential of generating deep blue uv radiation in the 200 nm or below.

The potential market for GaN based devices is predicted to be about 5B US \$.by 2009, and exploitation of white light sources about 12B\$.

9. Semiconductor Spintronics

Semiconductor Spintronics is an emerging field. These are electronic materials with combined semiconducting and magnetic properties. The aims are to integrate functionalities of semiconductor and magnetic materials. The spin of the electrons in the magnetic materials are being designed for a wide range of applications. In the long term, these materials could be used for quantum computing.

In ferromagnetic conductors the spins of the electrons are already being used in hard disk drive (Figure 12) in the read head market. The magnetic moments of the individual atoms spontaneously align themselves. There is also net alignment of the spins of the conduction electrons. This property has been

exploited in conducting ferroelectric materials in the form of a giant magneto resistance (GMR) for read head for hard disc drive. In the future Colossal Magneto Resistance (CMR) materials could replace GMR. CMR materials is an intensive area of material research.

One way in which it is possible to realize spintronics is to inject spin polarized current from metallic ferromagnets into semiconductors using ohmic contacts. Best ways are to dope semiconductors with ferromagnetic elements.

A wide range of room temperature ferromagnetic semiconductors have been reported, but it is still not clear whether these are homogeneous ferromagnetic semiconductors. Most of these are reported to be p type. There are interests to grow n type ferromagnetic semiconductors. There are interests also in doping other III - V semiconductors like the phosphides, antimonides with magnetic atoms. Figure 13 illustrates the principles involved in the development of spintronic materials.

Figure 13: Magnetic semiconductors for spintronics.



10. Materials for Health

In this part of the discussion, I would like to touch in a fairly general way, the role of materials for health. Materials for health is an extremely challenging field and present tremendous opportunities for innovation, research and development of useful devices for health monitoring, in advanced imaging for medical applications.

Materials for health generates a very high level of economic activities surpassing that of the electronic industries if one takes the contributions of the pharmaceutical industries to the world economy. Institutes of health and life science being set up practically in universities all over the world to conduct research in the synthesis, characterization and applications of nanomaterials for drug delivery, self health monitoring, cure for cancers, diabetes, Alzheimer's, tissue engineering ...

All types of materials are needed for advancement in medicines, medical devices, health care, bone implants, tissue engineering, drug delivery, health monitoring. We are all aware that the number of people approaching the greying generation is increasing rapidly. In UK alone hundred of thousands of people are benefiting from advancement in implants and tissue replacement. Innovative ways are being found to use a wide range of materials for bone and dental implants. Fracture of hip joint is common; hip may also become diseased – osteoarthritis. In such cases small lumps of bone are formed on the rubbing surfaces of the joint, which causes pain as the head rotates in the acetabulum as shown below :- 70

Figure 14: Schematic diagram of the human hip joints and adjacent skeletal components.



Figure 15: Left normal hip joint. Right fractured hip joint.



Orthopaedic implants require materials with diverse properties:-

- **4** Materials that do not age
- Materials that do not
- 🖊 Creep
- 4 Materials that do not
- ∔ Wear
- 4 Materials that do not
- Fatigue

Moreover, various types of biomaterials are used for implants ranging from calcium apaptite for bone, metals, ceramics, glasses, polymers, composites. See Figure 16.

Figure 16: Left shows a schematic diagram of a total hip replacement. On the right shows an X-ray picture of a total hip replacement.



11. Smart Polymer Implants

Smart polymer implants are being developed that can change shape in response to body's own chemicals. These smart polymer hydrogels could be used for

- Forming actuators as valves and switches for blood vessels switches
- drug release systems
- implants
- drug screening

Figure 17: Various parts of the body such as hip, knee arms that commonly require replacement.



Figure 18: Smart polymers implants being developed that can change shape in response to body own's chemicals.



It has also important applications in heart valves, and medical devices. These smart polymers have been developed by Prof Hans Jorg Schneider and his team at the University of Saarland in Germany. These polymers can operate automatically without the need of additional sensors, transducers, pumps. They do not need external additional power supply.

These polymers are prepared with diethylene triamine. A form of polymer was synthesized by reacting polymethyl acrylate and long- chain alkyl amines. Flexible polymers allow introduction of many different receptor functions.

Smart polymers have also been shown to produce sizeable dimensional changes with millibar concentrations of chemicals. A drug contained inside a microcapsule coated with the chemomechanical polymer can be released by external stimulation or by substances present in maligned tissues or blood such as in tumor tissue or by differences in pH.

12. Terahertz Imaging

I would like to say a few words about Terahertz imaging. What is Terahertz imaging? Terahertz region of the electromagnetic spectrum lies between 0.1 Terahertz to 10 Terahertz; 1 Terahertz (1 THz) is 10¹² Hz. What types of materials and techniques are used to produce and detect terahertz radiation? Are there any safety precautions which need to be strictly adhered to?

How is Terahertz imaging produced and measured? What issues still need to be resolved before Terahertz imaging becomes a routine tools like X-rays radiography, X Ray scanner, Nuclear Magnetic Resonance (NMR) imaging, ultrasound imaging. Materials play an important role as summarized in Figures 18 and 19.

Figure 19: The power as a function of frequency for different sources for Terahertz imaging. The region between 1-10 THz is known as the Thz gap. Recently some practical sources have become available.



13. Application of Terahertz Imaging

Although still in the early stage of development, the potential has already been demonstrated. Terahertz imaging is shown to be a very powerful imaging technique not only for security and semiconductor devices, but also for imaging soft materials like cancerous tissues and dental caries. Figures 20 & 21 show the usefulness of terahertz imaging.

Figure 20: A basal skin carcinoma is shown on the right and the reflected terahertz image is shown on the left. The image is obtained using a broadband 0.5 to 1.5 THz source. Cancerous tissue is easily detected accurately enabling the surgeons to remove only the diseased tissue. Courtesy of TeraView Ltd.



Figure 21: The THz time of flight image of a tooth with a number of caries on the right. The enamel and dentine region of the tooth can be differentiated. On the left, the THz absorption image of the same tooth showing clearly two caries (enclosed by rectangles) which will eventually lead to a cavity in the tooth.



13. Conclusions

I hope I have been able to convey in this presentation that advances in strategic materials act as engine of growth. They can generate tremendous economic activity and create wealth and prosperity for the country and the people. It is also shown that the development of advanced biomaterials improve the performance of bone implants, tissue engineering, drug delivery, medical imaging systems.

Moreover, advances in materials also have a beneficial effect in improving and providing affordable transportation, communication, and information technology. Advances in materials and materials engineering are also vital for the production of clean energy and the development of a sustainable economy, the protection of our environment and addressing issues of climate change.

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CRYPTOGRAPHY: CAESAR TO RSA

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Abstract: History of cryptography is as old as history of diplomacy and warfare. The word *cryptography* comes from Greek words Kryptos, meaning hidden, and Graphen, meaning to write. Cryptography was once the science and art of diplomatic and military communication. It was used to prevent disclosure of the contents of the messages between diplomatic positions and between army units. Use of cryptography later spread to civilian areas. With the advent of modern telecommunication, these methods began to be used even more heavily than at the beginning of its history. Whenever we use mobile telephone, the communication between the telecom transmitter and the handset is encrypted to prevent listening through other handsets. Similarly our e-mails can be encrypted. Secure Internet sites used for financial transactions transfer data in encrypted form.

Modern Communication



History of Cryptography

Cryptography probably began in or around 2000 B.C. in Egypt, where hieroglyphics were used to decorate the tombs of deceased rulers and kings. These hieroglyphics told the story of the life of the king and proclaimed the great acts of his life. They were purposefully cryptic, but not apparently intended to hide the text. Rather, they seem to have been intended to make the text seem more regal and important. As time went by, these writings became more and more complicated, and eventually the people lost interest in deciphering them.

Polybios Cipher

Perhaps the earliest cryptosystem was developed by the Greek historian Polybios (203-120 BC). He used a grid of letters where each letter of the message was replaced by the two numbers indicating the row and column in which the original letter lies. A Polybios square is the key for a Polybios encryption scheme. Here is a Polybios square with the English alphabet where I and J occupy the same square.

| | 1 | 2 | 3 | 4 | 5 | |
|---|---|-----|---|---|---|--|
| 1 | S | Y | D | W | Z | |
| 2 | R | I/J | Ρ | U | L | |
| 3 | Н | С | А | Х | F | |
| 4 | Т | Ν | 0 | G | Е | |
| 5 | В | K | М | Q | V | |

Replace letters with the pair of digits that indicates their column and row positions. For instance C = 23. The plaintext message I LOVE YOU is thus encoded as 22 52345554 213442.

Caesar Cipher

This encryption algorithm was supposedly used by Julius Caesar (100 - 44 BC) for transmitting his orders to his army. It is one of the simplest algorithms and too simplistic to be used for any serious communication. For a given alphabet, each character of the ciphertext is obtained by shifting a certain number of positions to the right of the alphabet in a cyclical manner. The key is the number of positions shifted. There are 26 keys including the obvious one.

| Α | В | С | D | E | F | G | Η | Ι | J | K | L | М | Ν | 0 | Р | Q | R | S | Т | U | V | W | Х | Y | Ζ |
|-----|-------|-----|------|----|----|----|-----|------|-----|-------|-----|------|-------|-------|------|-----|---|----|------------------|-----|------|-----|---|---|---|
| Е | F | G | Н | Ι | J | К | L | М | Ν | 0 | Ρ | Q | R | S | т | U | V | W | Х | Y | Z | А | В | С | D |
| The | e cip | her | text | ZM | RM | ZM | IHM | I ZN | 4GN | /I, w | hen | deci | rypte | ed, t | oeco | mes | | VI | INI [°] | VID | I VI | CI. | | | |

Cryptography in Literature

- *Journey to the Centre of the Earth* by Jules Verne
- The Adventures of Dancing Men, *The Return of Sherlock Holmes*, by Arthur Conan Doyle:

| ጟኇኯኯኯኯኯ | ፟ጚጚጞጞጞጞ | ጟፚጞጞ | ᠂ᡩ᠋ᡩ᠊ᡧ᠊ᡧ | ፞፞፞፝፞፞፞፞፞፞፞፞ጚጞጞጞ፞፞፝፞ጞ |
|-------------------|--|-----------------------|----------|-----------------------|
| 221 2 1 1 1 1 1 1 | $\mathcal{T}_{\mathcal{A}_{\mathcal{A}}}^{\mathcal{A}} \mid \Sigma \Omega \mathcal{N}$ | 254 52 $\sqrt{2}$ | エハアヘ | 77 ዲግ ፍ ፍ ሌ |

• The Da Vinci Code, a recent best-seller

Monoalphabetic Substitution cipher

This is much more sophisticated than the Caesar cipher. Each letter of the alphabet is uniquely substituted by anther letter. The table of substitutions forms the key. In the Roman alphabet, you can have 26! = 403,291,461,126,605,635,584,000,000 such keys. Guessing at the key is not very practical. Checking a million keys per second will take more than 12 trillion years, much longer than the expected destruction of our galaxy.

| Α | В | С | D | Е | F | G | Н | Ι | J | Κ | L | Μ | Ν | 0 | Ρ | Q | R | S | Т | U | V | W | Х | Y | Ζ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| М | Ε | R | 0 | С | U | Y | В | Q | W | F | т | Н | L | S | G | Ρ | Α | Х | J | Κ | D | Z | Ν | I | V |

The plaintext "kill the queen tonight" becomes FQTT JBC PKCCL JSLQYJ. If we decrypt XCC ISK SL XCGJCHECA CTCDCL QL ESXJSL, we get "See you on September Eleven in Boston".

Cryptanalysis

Cryptanalysis is the practice of changing ciphertext into plaintext without knowledge of the key. The Arabs were the first to make significant advances in cryptanalysis. An Arabic author, Abu Yusuf Yaqub ibn Ishaq al-Sabbah Al-Kindi, invented a technique for solving ciphers which is still used today. (He wrote 290 books on medicine, astronomy, mathematics, linguistics and music!) The technique is to

write down all the ciphertext letters and count the frequency of each symbol. Using the average frequency of each letter of the language, we can discover the correspondence between plaintext characters and ciphertext characters. This technique is powerful enough to cryptanalyze any monoalphabetic substitution cipher if a long enough ciphertext is provided.

Frequency Analysis

| Α | В | С | D | Е | F | G | Н | Ι | J | Κ | L | Μ |
|-----|-----|-----|-----|------|-----|-----|-----|-----|-----|-----|------------|-----|
| 8.2 | 1.5 | 2.8 | 4.3 | 12.7 | 2.2 | 2.0 | 6.1 | 7.0 | 0.2 | 0.8 | 4.0 | 2.4 |
| NI | 0 | - | ~ | - | ~ | _ | | | | | \ <i>\</i> | - |
| IN | 0 | Р | Q | R | S | Т | U | V | W | Х | Y | Ζ |

The table above gives the relative frequencies of different letters in the alphabet. This is based on a sample of about 100000 alphabetic characters taken from newspapers and novels.

Mary Queen of Scots

Mary Queen of Scots was imprisoned for 18 years and finally executed by Queen Elizabeth I. Cryptography and cryptanalysis played a major part in this piece of history

Mary Stuart, Queen of Scots, was born on December 8, 1542. She married Francis, Dauphin of France, son of Henry II on April 24, 1558. When Mary I of England died in the same year, Mary Stuart opposed the crowning of Elizabeth I. She was deemed a threat to the Crown and was imprisoned for 18 years. From the prison, Queen Mary had communicated to her friends about plots to assassinate Queen Elizabeth. Unaware of the breakthroughs made in cryptanalysis, she had encrypted her messages using monoalphabetic substitution cipher. QE1's secretary Sir Francis Walsingham used the Arabic techniques of cryptanalysis to decipher the contents of her messages and thus proved the charges of treason against Mary. Queen Mary was beheaded on February 8th, 1587.

Polyalphabetic ciphers

In order to make substitution ciphers more secure, more than one alphabet can be used. Such ciphers are called **polyalphabetic**, which means that the same letter of a message can be represented by different letters when encoded. Such a one-to-many correspondence makes the use of frequency analysis much more difficult.

| Α | В | С | D | Е | F | G | Н | Ι | J | Κ | L | Μ | Ν | 0 | Ρ | Q | R | S | Т | U | V | W | Х | Y | Ζ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Μ | Ε | R | 0 | С | U | Y | В | Q | W | F | Т | Η | L | S | G | Ρ | Α | Χ | J | K | D | Ζ | Ν | Ι | ۷ |
| L | Q | A | U | X | G | Ζ | S | Μ | С | Y | 0 | F | Ε | J | R | D | V | I | Ν | B | т | W | Ρ | K | Н |

The two alphabets are used alternatingly. "Attack at midnight" is now encrypted as MNJLRY MN HMOEQZBN. Note that a letter in the plaintext is represented by more than one letter in the ciphertext and vice versa.

The Vigenère Cipher

The Vigenère cipher is a polyalphabetic cipher, named after a 16-th century Frenchman called Blaise de Vigenère (1523 - 1596), based on using successively shifted alphabets, a different shifted alphabet for each of the 26 English letters. The procedure is based on the tableau shown below and the use of a keyword. The letters of the keyword determine the shifted alphabets used in the encoding process.

For the message COMPUTING GIVES INSIGHT and keyword LUCKY, we proceed by repeating the keyword as many times as needed above the message, as follows.

| L | U | С | ĸ | Y | L | U | С | ĸ | Y | L | U | С | ĸ | Y | L | U | С | ĸ | Y | L |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| С | 0 | M | Р | U | т | I | N | G | G | I | V | E | s | I | N | S | I | G | H | т |

For each letter of the message use the letter of the keyword to determine a row and go across the row to the column headed by the corresponding letter of the message. We illustrate this row-column look-up in Figure 3 for the first two letters of the message. The red arrows indicate the encoding of the first letter C and the green arrows the encoding of the second letter O. It follows that the first two letters "CO" in the message are encoded as "NI".

| | | | ¥ | | | | | | | | | | | | * | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|----|---|-----|---|---|
| 1 | A | B | С | D | E | F | G | H | L | J | K | L | M | N | 0 | P | Q | R | S | Т | U | ۷ | W | X | Y | Z |
| | В | С | D | E | F | G | H | - | - | K | L | M | N | 0 | P | Q | R | S | Т | U | ۷ | W | x | Y | Z | A |
| | С | D | E | F | G | H | 1 | J | K | L | M | N | 0 | Р | Q | R | S | Τ | U | ۷ | W | X | Y | Z | A | B |
| | D | E | F | G | H | 1 | J | ĸ | L | M | N | 0 | Ρ | Q | R | S | Τ | U | ٧ | S | × | Y | Z | A | B | C |
| | E | F | G | H | 1 | J | K | L | M | N | 0 | P | Q | R | S | Τ | U | ۷ | W | X | Y | Ζ | A | В | С | 0 |
| | F | G | H | L | J | K | L | M | N | 0 | P | Q | R | S | T | U | ٧ | Š | X | Y | Ζ | A | B | С | D | E |
| | G | H | - | J | K | L | M | N | 0 | P | Q | R | S | Τ | U | ۷ | W | X | Y | Z | A | B | С | D | E | F |
| | Н | 1 | J | K | L | M | N | 0 | P | Q | R | S | T | U | ٧ | W | X | Y | Z | A | В | С | D | E | F | 0 |
| | 1 | J | K | Ľ | M | N | 0 | Ρ | Q | R | S | T | U | ٧ | W | X | Y | Z | A | B | С | D | E | F | G | H |
| | J | K | L | M | N | 0 | P | Q | R | S | Τ | U | ٧ | W | X | Y | Z | A | B | C | D | E | F | G | H | 1 |
| | K | L | M | N | 0 | P | Q | R | S | T | U | ٧ | W | X | Y | Ζ | A | B | С | D | E | F | G | Н | L | J |
| > | L | M | N | 0 | P | 0 | R | S | Τ | U | ٧ | W | X | Y | Z | A | B | С | D | E | F | G | H | 1 | J | K |
| | M | N | 0 | P | Q | R | S | T | U | ٧ | W | X | Y | Z | A | B | С | D | E | F | G | H | 1 | J | K | L |
| | N | 0 | Ρ | Q | R | S | Τ | U | ٧ | W | X | Y | Z | A | B | С | D | E | F | G | H | 1 | J | K | L | N |
| | 0 | P | 0 | R | S | Т | U | V | W | X | Y | Z | A | В | С | D | E | F | G | H | L | J | K | L | M | N |
| | P | Q | R | S | Τ | U | ٧ | W | X | Y | Z | A | В | С | D | E | F | G | Н | L | J | K | L | M | N | 0 |
| | 0 | R | S | Τ | U | ٧ | W | X | Y | Z | A | B | С | D | E | F | G | H | 1 | J | K | L | M | N | 0 | F |
| | R | S | T | U | V | W | X | Y | Z | A | B | C | D | E | F | G | H | 1 | J | K | L | M | N | 0 | P | 0 |
| | S | Τ | U | ٧ | W | X | Y | Z | A | B | С | D | E | F | G | Н | 1 | J | K | L | M | N | 0 | P | 0 | R |
| | T | U | V | W | X | Y | Z | A | В | С | D | E | F | G | Н | L | J | K | L | M | N | 0 | P | 0 | R | 5 |
| > | U | ٧ | W | X | Y | Z | A | B | С | D | E | F | G | H | T | J | K | L | M | N | 0 | P | Q | R | S | 1 |
| | ٧ | W | X | Y | Z | A | B | С | D | E | F | G | H | 1 | J | K | L | M | N | 0 | P | Q | R | S | Т | ι |
| | W | X | Y | Z | A | B | С | D | E | F | G | н | P | J | K | L | M | N | 0 | P | 0 | R | S | Τ | U | 1 |
| | X | Y | Z | A | B | С | D | E | F | G | H | 1 | J | K | L | M | N | 0 | P | 0 | R | S | T | U | ٧ | ٧ |
| | Y | Z | A | B | C | D | E | F | G | H | 1 | J | K | L | M | N | 0 | P | 0 | R | S | T | U | V | W | X |
| | 7 | - | R | C | n | F | E | C | H | 1 | 1 | V | 1 | - | H | 0 | D | 0 | D | 0 | T | i. | W | 100 | Y | 1 |

| L | U | С | Κ | Y | L | U | С | K | Y | L | U | С | Κ | Y | L | U | С | Κ | Y | L | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|--|--------------------|
| С | 0 | M | Ρ | U | Т | T | N | G | G | | ۷ | Ε | S | I | Ν | S | T | G | Н | Т | | <==MESSAGE |
| Ν | I | 0 | Ζ | S | Ε | С | Р | Q | Ε | Т | Ρ | G | С | G | Y | Μ | К | Q | F | Ε | | <==Encoded Message |

Note that the letter I in the message corresponds to four different letters in the encoded message. Also in the encoded message the letter E was substituted for two different letters of the original message. Such many-to-one substitutions make letter frequency counting much more difficult. For many years Vigenère's system was called "the indecipherable cipher".

When the encoded message is received, it is decoded by reversing the process. Go across the top row to the column headed by the letter in the keyword. Now go down that column until you come to the corresponding letter in the encoded message. The correct letter in the original message is found by proceeding to the left across the row containing the letter in the encoded message. Again let our keyword be LUCKY and let the encoded message be XUVRG DYXOP JQJO PP. Using the tableau, we

column-row look-up as described above to decode XUVRG DYXOP JQJO PP as MATHISEVERYWHERE.

Ironically, when Mary Queen of Scots used monoalphabetic substitution cipher to encode her communication, Vigenère cipher was already in use. If Mary had known about it and used it instead, Sir Francis would not have been able to decrypt her messages.

Le Chiffre Indéchiffrable

For 300 years the Vigenère cipher was considered to be practically unbreakable. Breaking *le chiffre indéchiffrable* is attributed to Charles Babbage (1854) and Friedrich Kasiski (1863), a Prussian military officer. The idea is to look for repeated phrases and their spacings in the ciphertext to determine the length of the keyword and then divide the message into a simpler form to which letter frequency analysis could be applied.

The Index of Coincidence

The index of coincidence is a statistical measure of text which distinguishes text encrypted with a simple monoalphabetic substitution cipher and more complicated polyalphabetic ciphers such as Vigenère cipher. It was discovered by Philip Friedman and published in 1920, in the article *The Index of Coincidence and its Applications in Cryptography*, Riverbank Publications Number 22. David Kahn (*The Codebreakers*, MacMillan, New York, 1968) called this paper "the most important single publication in cryptology."

To determine the index of coincidence of a piece of text, take the text and shift it by some random number of places (wrapping around if necessary) and write the shifted and unshifted texts next to each other:

```
Althoughthecipherisinscrutableandoftenunforgeabletoanyonewithoutthis
oftenunforgeabletoanyonewithoutthisAlthoughthecipherisinscrutableand
x x x x x x
```

Now count the number of coincidences – that is, the number of places in which the same letter occurs in both strings of text. In this example, the coincidences are marked with an "x". There are 4 coincidences for 68 characters of text, a rate of about 4/68, or approximately 6 percent.

Using the standard frequencies with which individual letters appear in English text, the probability that a coincidence will occur is around 6.6 percent. On the other hand, if the text is random, and the different letters are chosen with equal probability, the probability of a coincidence is much smaller (around 3.8 percent). The most important property of the index of coincidence is that it is the same for text encrypted with a simple substitution cipher as for plain text.

Breaking the Vigenère cipher

To illustrate the usefulness of the index, suppose we receive a message encrypted by the Vigenère cipher. If the keyword for the cipher has N characters, then the cipher message can be split up into N subsets (the first subset has letters 0, N, 2N,...; the second has letters 1,N+1,2N+1,...; and so on.) Each of these subsets has been encrypted with a simple substitution cipher corresponding to a fixed column of the Vigenère tableau.

To find "N" using the index of coincidence, we compute the index of coincidence of the text with itself shifted by an integer k, for different values of k. When we choose k a multiple of N, the index should jump from the "random value" of about 3.8 percent to the "English" value of around 6.6 percent.

For example, the following string of text was encrypted with the Vigenère cipher:

```
TPCTY LVEOO GBVRC BTWXS IHDKD QIRVQ QUKWL TMNQO EKMLP AURKL VHIUX YJRNV
QWJEK UEQVD IXPLU RKLVT QSLKI LWAZI JWXPL QRKIO PWFME XLLCP KDIKV EUXYX
EAAQV MEKVN AVZRQ JGEMX LQUPM PCRLO IZPZZ FPONI AYPVQ RMVHC QZFLV IKGUK
LRXER MDWVG RVMPQ PWLWT TIYEQ JAYMK XBPUK PZJBF WIRKS QJMSV FYKFP QLRXE
OIPID IQQLI ICPFP LMVBR BUAMW KLLUM FLRXE CDQFV IKNWZ KUIXF BTIII CQZQM
JQVUX UVZXL XMDAY IIOMP AZXEK VYIDC EGIDX NMQJQ ZQVMP FMESC EQGQD IDIJD
MDXYI ACGES WSIFQ YIUMQ CBQSE EINBT CNSOM AUQLW BQVFL VALTS AJKLV JIZHJ
```

```
MPVZQ XTLCQ ZFLDC ECVPW LRQQB TIVQV UWGPK LFTAF IKLXH BQVKL BGIEE KLFTA
FCCEK FAQPR LEGID QVWMG MPMCC LNWDH DCPRQ DMKJX KTQXY LFFMZ SKXEA NMGVJ
OQUYI CIPVQ NICMH GCZXF XEGUF LRXDQ LAAEM KVWFL VTFVK MYJIJ GBALV EOVPK
PFZFP OWMEH KGAEM EXEGU AVEMK INAVZ RQJMQ HFMQT CEXTE RUMYI KSHPW IXYIT
CGILV VBKVU WYSRN LIECO CQZUP ZJQWX YCJSR NCZXF XEGMP ICMSG ZYIFP LTLRV
FQJKV QIEIJ KMEMW PBGCZ XFXEG MFSYM AGUQX VEZJU QXFHL VPKAZ PIHWD XYSRC
ZFQPK LFBTC JTFTQ FMJKL QLXIR HJGQZ XFXEG TMRUS CWXDM XLQPM EWHYF ESQRD
ILNWD HWSOV PKRRQ BUAMO VJLTB TCIMD JBQSL WKGAE WROBD ZURXQ VUWGP FYQQN
FVFYY NMMRU SCVPK QVVZA KGXFJ COQZI VRBOQ QWRRA FMEXI SVCTX XYIJV PMXRJ
CNQOX DCPQC XJFVF CUFLP WBTDM RK
```

Here are the values of the index of coincidence for various shifts of the text.

| Shift | Index | | | | | | | |
|-------|-------|-----|------|------|----|-----|-----|----------|
| 1 | .028 | | | | | | | |
| 2 | .045 | | | | | | | |
| 3 | .034 | | | | | | | |
| 4 | .037 | | | | | | | |
| 5 | .042 | | | | | | | |
| 6 | .035 | | | | | | | |
| 7 | .070 | (*: | This | must | be | the | key | length!) |
| 8 | .032 | | | | | | | |
| | | | | | | | | |

Notice that the key length N pops out as the high value of the index of coincidence.

Once we know "N", we attack the N subtexts of the message by frequency analysis. If the message is in a true Vigenère cipher, this is extremely easy, since each column of the Vigenère tableau is just a rotation of the usual alphabet, and once we get one letter correct, we know them all. A number of Java applet implementations are available for the Vigenère cipher on the Web.

The Zimmermann Telegram

On January 9, 1917, the German Supreme High Command held a momentous meeting. Previously, they had agreed that U-boats must surface before firing their torpedoes, a restriction that would reduce accidental attacks on civilian shipping, but now German commanders were about to agree on a course of all-out U-boat aggression, set to begin on February 1. Although such a change of policy would cut off supply lines and possibly starve Britain into submission within six months, there was a risk attached to this strategy. Up until this point, President Woodrow Wilson had kept America neutral, but the inevitability of civilian casualties resulting from all-out U-boat aggression threatened to draw America into the war. Consequently, the German Foreign Minister, Arthur Zimmermann, decided to draw up an insurance policy.

Zimmermann sent a telegram to Heinrich von Eckardt, the German ambassador in Mexico via German Embassy in Washington, stating that in the case of America entering the war, Germany would support a Mexican invasion of America, helping it to reclaim territories such as Texas, New Mexico and Arizona. If Zimmermann's plan worked, then America would be too busy defending itself at home to become involved in the European conflict. Ideally he would have sent the message via Germany's own transatlantic cables, but on the first day of the war, the British had severed Germany's transatlantic cables. This act of sabotage forced Zimmermann to send his telegram via cables that touched Britain.

Zimmermann had encrypted the telegram, and assumed that the German codes were strong enough to protect his message, but he underestimated the skills of the British codebreakers. The people at Admiralty's codebreaking office, known as Room 40, were well versed in cracking a whole variety of codes. Although Room 40 rapidly deciphered the Zimmermann telegram, the British did not immediately show it to the Americans. If the Americans entered the war because of the hostile contents of the telegram, then the Germans would realise that their diplomatic code had been broken, and they might then upgrade their codes, depriving the British of a valuable source of intelligence. Furthermore, unrestricted U-boat warfare was due to begin in just a matter of days, and this in itself might provoke the Americans into entering war. Why risk losing a source of intelligence, if the Americans might already be on the verge of joining the Allies? On February 1, Germany embarked on its strategy of unrestricted U-boat warfare, but two days later President Wilson announced to Congress that America would continue to remain neutral.

This left the British with no choice but to reveal the contents of the Zimmermann telegram. They did not want Germans to know that their code was broken, nor did they want Washington to know that their diplomatic communications were tapped by the British. So they arranged one of their espionage agents in Mexico to get a copy of the telegram and presented it to the Americans. At first, there was skepticism about the authenticity of the telegram, but in a surprising move, Arthur Zimmermann admitted that he did indeed send the telegram.

At the beginning of the year Wilson had said that it would be a "crime against civilisation" to lead his nation to war, but the Zimmermann telegram forced him to change his mind: "I advise that the Congress declare the recent course of the Imperial Government to be in fact nothing less than war against the government and people of the United States, and that it formally accept the status of belligerent which has thus been thrust upon it."

A single breakthrough by Room 40's codebreakers had succeeded where three years of intensive diplomacy had failed.

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| 23571 | 17504 | 11269 | 18276 | 1810 | 1 0317 | 0228 | 17.694 | 4473 | 5 |
| 23284 | 22200 | 19452 | 21589 | 6789 | 3 5569 | 13918 | 8 8958 | 1213 | 57 |
| 1333 | 4725 | 4458 | 5905 1 | 7166 | 13851 | 4458 | 17149 | 14471 | 6700 |
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A OLD TELEGRAM RECEIVED.ar By Much & Ech Loff autimit FROM 2nd from London # 5747. Bone Oct. 27,195'1 "We intend to begin on the first of February unrestricted submarine warfare. We shall endeavour in spite of this to keep the United States of america neutral. In the event of this not succeeding, we make Mexico a proposal of alliance on the following basis: make war together, make peace together, generous financial support and an understanding on our part that Mexico is to reconquer the lost territory in Texas, New Mexico, and arizona. The settlement in detail is left to you. You will inform the President of the above most . secretly as soon as the outbreak of war with the United States of America is certain and add the suggestion that he should, on his own initiative, Japan to immediate adherence and at the same time mediate between Japan and ourselves. Please call the President's attention to the fact that the ruthless employment of our submarines now offers the prospect of compelling England in a few months to make peace." Signed, ZHERERAR.

One-time pad

One-time pad is an encryption algorithm which has been proven, from theoretical first principles, to be unbreakable when properly deployed. Here the plaintext is encoded with a random Vigenère cipher key as long as the plaintext. For the code to be secure, one should resist the temptation to reuse the pad. Totally random key results in provably unbreakable encryption. Presence of recognisable words can weaken the system. One-time pad was used for top secret communication such as that between heads of state of USA and USSR. One of the major difficulties in using one-time pad is the logistical problems of key distribution.

The Enigma

Albert Scherbius (1918) invented a cipher machine with rotating rotors which the German military adapted and called the Enigma machine. At first appearance it looks like a funny looking typewriter.

Breaking the Enigma is accomplished in part by Marian Rejewski (early 1930's), a Polish mathematician at Biuro Szyfrow (who was lucky enough to get a working model of the machine) and
Alan Turing (1912 – 1954) an employee at the Government Code and Cipher School at Bletchley Park. Turing invented and used a code-breaking machine called *bombe*.



Post-war Cryptography

During the post-war period computers began to perform far more complex encryption at much faster pace. Computer scrambles numbers instead of letters of the alphabet. Numbers, letters and other characters are transformed into binary digits. These digits are then encrypted.

In the early 1970's Horst Feistel, working for IBM developed the Lucifer encryption system. The binary form of the message is split into blocks of 64 digits. Digits in each block are shuffled, split into half-blocks of 32 and the right half is put through a mangler function, a complex substitution scheme. This is added to the left, creating a new right while the old right is labeled as a new left. The procedure is repeated 16 times. The details of the mangler function determine the key.

Data Encryption Standard

The number of possible keys for the Lucifer encryption system was a crucial issue with the US government. Its National Security Agency argued to limit the number of keys so that only they can break the code. (NSA employs more mathematicians and cryptologists than any other organization.) On November 23, 1976, the 56-bit version of Lucifer was officially adopted as the US standard for encryption and it was named DES. It has roughly 10¹⁷ (100 million billion) keys.

The Key Distribution Problem

Distribution of the decryption key remained the biggest problem. If the key itself is encrypted and sent, naturally that would need another key. To avoid interception, executives hand-carried keys to the destination, often in suitcases chained to their wrists. Many thought that the key distribution problem is theoretically unsurmountable. The first ideas towards solving the key distribution problem were put forward by Whitfield Diffie and Martin Hellman in 1976.

Modular Arithmetic

The method Diffie and Hellman came up with was based on modular arithmetic. Modular arithmetic is the usual addition, multiplication and exponentiation modulo a given integer. It is easy to do, hard to undo. An example is given below.

 $3^7 \pmod{11} = 27 \pmod{11} \times 27 \pmod{11} \times 3 \pmod{11} = 5 \times 5 \times 3 \pmod{11} = 5 \times 4 \pmod{11} = 9$

If Alice and Bob want to exchange a key, each chooses a number (*A* and *B*) and keeps it a secret. There are two system parameters *P* and *Y*. *P* is a large prime number and *Y* is an integer less than *P* with the property that $Y^n \pmod{P}$, $1 \le n \le P - 1$ will produce all numbers from 1 to P - 1. That there will always be such a *Y* for any prime *P* is a result in number theory.

Alice calculates $a = Y^A \pmod{P}$ and Bob calculates $b = Y^B \pmod{P}$. These numbers are sent to each other. Alice calculates $b^A \pmod{P}$ and Bob calculates $a^B \pmod{P}$, both getting Y^{AB} . This common value is agreed to be the key. Eve, the eavesdropper, may know the values of *Y*, *P*, *a* and *b*, but cannot know *A* and *B*. As modular arithmetical operations are not reversible, Eve cannot work back to get the values of *A* or *B*, if the numbers involved are large. This is called the Diffie-Hellman-Merkle key exchange system.

Public Key Cryptography

Even though the key exchange system described above is a major breakthrough, it is still tedious and inconvenient as it takes a few messages to be sent back and forth before a key is agreed on. In addition, there is no authenticity verification tool built into the Diffie-Hellman system. Both of these problems were solved when, in April 1977, Ronald Rivest, Adi Shamir and Leonard Adleman invented the public key cryptographic system that became known as the RSA system. Instead of having a single key, the receiver of the message has a public key and a private key. Public key is publicised while the private key is kept secret. If Alice wants to send Bob a message, she encrypts it using Bob's public key. Bob decrypts the message using his private key. Knowledge of the public key is not enough to decrypt.

Theory behind RSA

If Alice wants to choose private and public keys so that Bob and others can send her secret messages, she picks two very large prime numbers p and q. Alice multiplies these two numbers to get N = pq. She now picks another number e that has no common factors with (p-1)(q-1). N and e form the public key while p and q form the private key.

To encrypt a plaintext message M < N, Bob calculates $C = M^e \pmod{N}$ and sends it over to Alice. Alice works out the decryption key by solving the equation $ed = 1 \pmod{(p-1)(q-1)}$. This is accomplished by a technique known as Euclid's algorithm. It need be done only once and does not depend on the cipher text. To decrypt, Alice calculates $C^d \pmod{N}$ and recovers M.

$$C^{d} (\mathrm{mod} n) = \left(M^{e}\right)^{d} (\mathrm{mod} n) = M^{ed} (\mathrm{mod} n) = M$$

Without the knowledge of *d*, the intercepted message cannot be decrypted. With large encryption block sizes, methods such as frequency analysis are useless.

Prime Factorisation

If everybody knows N why can't they just factorise it to get p and q? The security of RSA code hinges on the fact that we do not have a fast algorithm to factorise integers. If the prime numbers involved are very large, it becomes too time consuming to factorise. Rivest estimated that factoring a 125 digit number which is the product of two 63 digit prime numbers would require at least 40 quadrillion years using the best factoring algorithm known, assuming that ab (mod c) could be computed in 1 nanosecond, for 125 digit numbers a, b, and c.

Conclusion

This is the current state of cryptography. RSA is currently the most commonly used encryption system. It is believed that breaking RSA is equivalent to finding a fast algorithm for prime factorisation. Other cryptosystems like quantum cryptography are in the pipeline. While public-key cryptography relies on the computational difficulty of integer factorisation, quantum cryptography relies on the laws of quantum mechanics.

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