SELECTIVE ISOLATION OF HEAVY METAL IONS USING IMMOBILIZED THIACROWN ETHERS

Bahruddin Saad*, Chong Ching Ching, Abdussalam Salhin Mohamad Ali, Ismail Ab Rahman, Norita Mohamad and Muhammad Idiris Saleh

School of Chemical Sciences,

Universiti Sains Malaysia, 11800 Penang,

Malaysia

Abstract

Sorbent materials based on three thiacrown ethers, 1,4,7,10-tetrathiacyclododecane (12S4), 1,4,7,10,13-pentathiacyclopentadecane (15S5) and 1,4,7,10.13,16-hexathiacyclooctadecane (18S6) were prepared by immobilizing the ligands into sol gel matrix and coating on commercial fluorisil particles. The competitive sorption characteristics of a mixture of eleven metal ions (Mg^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ca^{2+}, Cu^{2+}, Ni^{2+}, Ag^{+}, V^{4+}, Hg^{2+}) using (i) batch method using ligands trapped in sol gel (SG) matrices and (ii) off-line solid phase extraction (SPE) column containing the fluorisil coated ligands were studied using ICP-MS. SG sorbents were characterized by FTIR, EDX and TGA/DTG. The metal extraction were optimized for key parameters such as pH, contact time/ flow rate, particle size (for SG sorbents) and ligand concentration. Under the optimized conditions, all the immobilized thiacrown ethers exhibited high selectivity towards Ag^{+}, with slight responses to Hg^{2+} and Cu^{2+} (% extraction) while the extraction of other studied metal ions were negligible. The sorbents can be repeatedly used three times as there was no noticeable deterioration in the metal uptake or interference from other metal ions. These sorbent materials, expecially the

SPE type, can be recommended for the selective isolation and preconcentration of traces of Ag^{+} from natural water samples.

Keywords: Thiacrown ethers, sol gel, solid phase extraction, heavy and transition metal ions.

1. Introduction

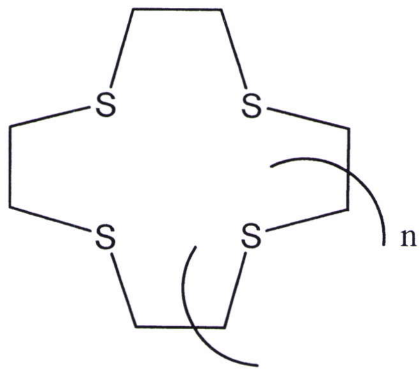
Thiacrown ether is one of the classes of crown ethers in which the donor oxygen atoms on the macrocyclic ring are partially or totally replaced by sulfur atoms.[1,2] Thiacrown ether is classified as soft Lewis base and it is well known to interact selectively with soft metal ions such as Ag^{+}, Hg^{2+}, Cu^{+} and Pd^{2+}.[3,4] Therefore, thiacrown ether and its derivatives have been actively studied for the selective separation of soft metal ions.

Conventional separation method, namely liquid-liquid extraction (LLE) using thiacrown ethers has been extensively studied over the years.[5-8] However, this method is subjected to several limitations such as being time consuming, labor intensive, use of large amounts of organic solvents and difficult separation caused by formation of emulsion.[9,10] The steady increase in the use of solid phase extraction (SPE) which can overcome the disadvantages of the LLE, has aroused much interest. SPE offers several distinct advantages namely, repeated use and amenable to automation.[10,11] This is achieved by the immobilization (physical or chemical) of functional groups and ligands onto various supports such as silica gel[12,13], amberlite XAD[14,15], activated carbon[16], metal alkoxide glass[17,18] and silica modified column or disk[19,20].

Several reports on the immobilization of thiacrown ether and its derivatives have been published. Bruening *et al.*[12], has chemically bonded 1,4-dithia-19-crown-6 and 1,4,7,10-tetrathia-18-crown-6 onto silica gel, which was subsequently used for the preconcentration of Pd^{2+}, Au^{3+}, Hg^{2+} and Ag^{+} using column method. Moyer *et al.*[21] has physically immobilized tetrathia-14-crown-4 on the cation exchange bead for the batch extraction of Cu^{2+}, while Bagheri and Shamsipur have immobilized the pentathiacrorwn-15-crown-5 and hexathia-18-crown-6-tetraone onto C_{18} membrane disk for the preconcentration of Au^{3+} and Hg^{2+}.[19,20]

Sol gel is a porous glass-like material produced from organometallic compounds at low temperature in which the complexing ligand can be immobilized to provide the solid phase. During extraction, small analytes can diffuse into the pores of the sol gel matrix and interact with the trapped ligand.[22] The crown ether, 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7,16-bis(malonate) immobilized sol gel matrix for the selective separation of Sr^{2+} was first demonstrated by Yost *et al.*[23]

In this report, three cyclic thiacrown ethers, namely, 1,4,7,10-tetrathiacyclododecane (**12S4**), 1,4,7,10,13-pentathiacyclopentadecane (**15S5**), 1,4,7,10,13,16-hexathiacyclooctadecane (**18S6**) (**Figure 1**) that were physically immobilized into two different types of supports namely sol gel matrix (sorbents referred to as 12S4-SG, 15S5-SG and 18S6-SG) or coated onto the surface of commercial florisil silica particles (sorbents referred to as 12S4-SPE, 15S5-SPE and 18S6-SPE). The resulting materials were used for the selective removal of traces of heavy metal ions using two approaches, i.e. (i) batch-wise for the case of sol-gel immobilized ligands, and (ii) column for the case of coated fluorosil particles. Key factors that contribute to the extraction such as equilibrium time, pH, ligand and metal ion concentration, foreign metal ions and reusability of the solid support were investigated.



n=1, 12S4
n=2, 15S5
n=3, 18S6

Fig 1. Chemical structure of thiacrown ethers studied.

2. Experimental

2.1 Apparatus

A Perkin Elmer 6100 inductively coupled plasma-mass spectrometry (ICP-MS) with version 2.0 software was used. The instrument conditions and general method parameters are listed in **Table 1**. FTIR spectrum (4000.0-400.0 cm^{-1}) in KBr were recorded using Perkin Elmer 2000 FTIR system. LEO Supra 50vp field emission scanning electron microscope (SEM) equipped with Oxford INCA 400 energy dispersive x-ray microanalysis system (EDX) was used to study the surface morphology and semi-quantitative analysis of the sol gel. Voltage? Thermogravimetric analysis (TGA) was performed with Perkin Elmer thermogravimetric analyzer TGA 7 and differential thermal analysis (DTG) with Perkin

Elmer Differential Scanning Calorimeter Pyris 1 DSC using a heating rate of 10 $Cmin^{-1}$ under nitrogen atmosphere. An Orion ion analyzer model WA940 was used for pH measurements. A mechanical shaker (Stuart Scientific, UK) was used for extraction and de-ionized water was produce from Millipore Milli-Q plus.

Table 1: ICP-MS instrumental operating conditions and data acquisition parameters

Condition / parameters	Result
ICP parameters	
R.f. power (W)	1000
Coolant argon flow rate (L min^{-1})	15
Auxiliary argon flow rate (L min^{-1})	1
Nebulizer argon flow rate (L min^{-1})	97
Operating frequency (MHz)	40
Sample introduction system	Cross flow nebulizer
Sample cone	Nickel with a 1.1 mm orifice
Skimmer cone	Nickel with a 0.9 mm orifice
Scanning mode	Peak hopping
Pressure (quadrupole analyzer) ICP (Torr)	4.18×10^{-5}
Number of replicate	2

2.2 Chemicals and reagents

Stock solution (100 ppm) containing mixture of metals (sulfates of Zn^{2+}, Cd^{2+}, V^{4+}, Ni^{2+}, Cu^{2+}, Mn^{2+}; nitrates of Mg^{2+}, Co^{2+}, Ag^{+} and chloride of Hg^{2+} in a final volume of 250 mL were prepared by dissolving appropriate amount of metal salt in 2% w/v HNO_3 solution. A 1M sodium acetate (Riedel-de Hean) solution was prepared by dissolving 34.02 g of the salt in 250 ml de-ionized water.

Thiacrown ethers, 12S4, 15S5 and 18S6 (Aldrich) were used without further purification. Tetraethoxysilane (TEOS) from fluka was used as sol gel precursor and Florisil 3ml column was purchased from IST. Other solvents including ethanol (EtOH) (Systerm), tetrahydofuran (THF) (Fisher Scientific) , 1.2-dichloroethane (Merck), HCl (Fisher Scientific) and HNO_3 (Merck) were used as received.

The real water samples, namely, tap water, rain water, river water (Waterfall River) and lake water (Youth Park), Penang, Malaysia were collected and filtered to remove suspended particles before use.

2.3 Synthesis of sol gel immobilized thiacrown ethers

The sol solution was prepared by stirring a mixture of 3.28ml TEOS, 4.56ml EtOH, and 0.35ml HCl (4M) for 15 min. Thiacrown ether (12S4, 15S5 and 18S6 respectively) which has been dissolved in THF was then added separately to the sol solution and stirred vigorously for 45 min. The resulting clear and homogeneous solution was aged in 60°C oven for 2 days. In drying stage, shrinkage of the gel occurred and the gel cracked. The gel then was soaked in de-ionized water for 1 day to condition the material. After that, the gel was dried at 60°C for 1 day and ground into small pieces (1-5mm in diameter) before it was ready for extraction. Blank sol gel was prepared following the same procedure in the absence of the thiacrown ether.

2.4 Column preparation and conditioning

The column method was performed with 3ml column containing 100mg of FL silica, purchased from IST. First, the column was washed with 10ml of methanol, 5ml of HNO_3 (0.1M) and 10ml water alternatively to remove contaminants. After drying the column by passing air through, 2ml of thiacrown ether ligand in 1,2-dichloroethane was loaded into the column, and was drawn slowly through the silica column by applying a slight vacumn. Finally, the immobilized column was dried in 60°C oven to evaporate the solvent before it was ready for extraction.

2.5 Extraction and preconcentration of metal ions

The batch method was conducted with sol gel immobilized thiacrown ether while the off-line preconcentration was carried out with Florisil silica column immobilized thiacown ether.

2.5.1 Batch method

In the batch method, 0.5g of sol gel was placed in a glass vial along with 5ml of a mixture of metal ions solution. The mixture was shaken mechanically at room temperature (25°C) for 30 min. After the equilibrium time, the mixture was filtered and the unextracted metal ions in the filtrate were determined by ICP-MS. Once the loading is completed, the sol gel was regenerated by shaking it with 10ml of 1M HNO_3, stripping the extracted metal ions.

After that, the sol gel was rinsed several times with de-ionized water and dried in 60°C oven before the next extraction cycle was conducted.

2.5.2 Column method

The thiacrown ether loaded column was first wetted with 5ml of water, then the sample solution containing 2.5ppm of Ag^+ was passed through the column. After the extraction, the Ag^+ was stripped from the column with 10ml of 0.5M HNO_3 and determined by UV spectrophotometer.

3. Results and discussions

3.1 The effect of solvent on the sol gel immobilized thiacrown ether

Due to the poor solubility of thiacrown ether in polar solvent such as H_2O and EtOH, various solvents, namely, chloroform, acetonitrile, 1,2-dichloroethane and tetrahydrofuran have been tested. When chloroform, acetonitrile and 1,2-dichloroethane were used, inhomogeneous of sol solution and leaching of thiacrown ether from the sol gel occurred. However, tetrahydrofuran was able to produce a homogenous sol gel. Therefore, THF is a suitable solvent in preparing the thiacrown ether sol gel.

3.2 FTIR analysis

The FTIR spectrum of free thiacrown ether ligands (12S4, 15S5 and 18S6), blank sol gel and sol gel immobilized thiacrown ether are shown in **Figure 2**. For the free thiacrown ether, the characteristic absorption band appearing at 620cm^{-1} is produced by C-S bond, while the S-CH_2 bond appears at 1433 cm^{-1}, 1419 cm^{-1} and 1384 cm^{-1} for 12S4, 15S5 and 18S6 spectra respectively[24].

Generally, both of the blank and thiacrown ether sol gels exhibit similar spectra. The presence of a broad and intense absorption band for all the sol gel spectrum between 1350 and 1000 cm^{-1} with maxima peak at approximately 1083 cm^{-1} is assigned to the Si-O-Si bond. Meanwhile, the bands around 793 and 470 cm^{-1} are resulted from Si-O vibration.[25] The bands around 3400 and 1618 cm^{-1} are due to the deformation mode for OH group and molecular water, whereas the silanol group (Si-OH) shows an absorption at 949cm^{-1}.[26,27] Of all the thiacrown ether-sol gel spectrum, neither C-S nor S-CH_2 peak appears as observed in the free thiacrown ether spectrum. Therefore, FTIR spectrum are unable to provide strong evidence to ascertain the presence of thiacrown ether in sol gel matrix.

3.3 EDX analysis

The EDX results of the free thiacrown ether ligand, blank sol gel and sol gel immobilized thiacrown ether was summarized in **Table 2.**

Table 2. EDX results of free thiacrown ether, blank sol gel and thiacrown ether sol gel.

Element	(%)				
	Thiacrown ethter ligand	Blank Sol Gel	12S4 Sol Gel	15S5 Sol Gel	18S6 Sol Gel
Carbon	39.96	20.99	5.47	5.12	4.78
Oxygen	-----	35.82	44.45	55.59	47.97
Silicon	-----	43.19	48.55	39.20	46.45
Sulfur	53.34	-----	1.55	0.74	0.80

Firstly, the analysis on the free thiacrown ether ligand revealed that carbon and sulfur are the main elements in this ligand with the composition of 39.96% and 53.34% respectively.

For the blank sol gel, the main elements are Si (43.19%) and O (35.82%). This result well agrees with the FTIR spectra of the blank sol gel, in which the Si-O-Si is the backbone of this material. Since thiacrown ether is absent in the blank sol gel, no sulfur is detected.

Further analysis on 12S4, 15S5 and 18S6 sol gel show that, apart from the major elements such as Si, O and C, sulfur are also detected with 1.55, 0.74 and 0.80% for 12S4, 15S5 and 18S6 sol gel respectively. Therefore, it can be concluded that thiacrown ether is present in the sol gel matrix.

3.4 Thermogravimetric analysis

The thermogravimetric analysis (TGA) was done on the free thiacrown ethers (12S4, 15S5 and 18S6), blank sol gel, sol gel immobilized thiacrown ethers, and used sol gel immobilized thiacrown ether. The analysis was conducted from 30°C to 700°C in nitrogen atmosphere at the heating rate of 10°C/min.

From the TGA thermogram, all the three thiacrown ethers generally decompose in only one step (**Figure 3**). The differential thermal analysis (DTG) curves show that the decomposition of these thiacrown ethers is an endothermic process. The ligands lose almost all of their weights (>99%) at 280°C, 330°C and 340°C respectively (**Table 3**). The trend of the thermogram also shows the correlation between the size of thiacrown ether and decomposition temperature. Gradually increase in the decomposition temperature have been observed.

3.4.1 Blank sol gel

The thermogram of the blank sol gel shows three distinct steps of weight loss (**Figure 4A**). The first loss which takes place below 200°C is associated with the physical desorption of water and the evaporation of ethanol. This indicates that the water preferentially adsorbed on the surface of silanol sites.[28,29] A very broad endothermic peak (236 to 635°C) occurs in the second step. This is probably due to the evaporation of trapped H_2O molecules in the silica, which requires significant thermal energy to release it.[27] Another possible explanation is the combustion of organic components such as carbon, hydrogen and oxygen.[30] After that, a sharp endothermic peak is observed at 660°C. However, this peak is not accompanied by the great weight loss (1.53%) as compared to the first and second decomposition steps which contribute to the 13.41% of weight loss (**Table 3**). Therefore, it can be concluded that the sol gel produced is a thermal stable material because 84.81% of the total weight is still retained by 700°C.

3.4.2 Sol gel immobilized thiacrown ethers

The sol gel immobilized thiacrown ethers generally exhibit the same thermal profile with the blank sol gel (**Figure 4B-D**). The three sol gel loss approximately 10.4, 8.9, and 9.7% weight below 200°C, which associated with the loss of the physical desorption water, as the case for the blank sol gel. There is no significant weight loss at temperature between 280°C and 340°C as observed in the free thiacrown ethers thermogram (**Figure 3**). This indicates that the thiacrown ethers still retain in the sol gel matrix and do not decompose at their own decomposition point. The sharp endothermic peak observed at 600°C for the blank sol gel was affected by the addition of the thiacrown ether ligands. This peak appears at 460 and 620°C with the weight loss of 6.9 and 1.4% for 12S4 and 15S5 sol gel respectively. For the 18S6 sol gel, this peak fall outside the range (>700°C) of the heating. In conclusion, the immobilization of thiacrown ethers in sol gel matrix do not affect the stability of the material as the final weight of these three sol gels at 700°C are about the same with the blank sol gel.

3.4.3 The used sol gel immobilized thiacrown ethers

In order to ascertain the stability of the sol gel, the thermal analysis were conducted on the sol gel after shaking with metal ions solution. From the thermogram, the first decomposition step seems to cover greater temperature range (30°C to 528°C) and the endothermic peak becomes wider (**Figure 5**) which is probably due to the increase of the water content in the sol gel. After extraction with metal ion, two doublet sharp endothermic peaks have been observed. The first peak was appeared after heating up to 550, 580 and 550°C with the weight loss of 11.1, 32.8 and 15.2% for the three thiacrown ether sol gel respectively, corresponding to the loss of the metal ion salt trapped by the sol gel.[31] The second peak at 590°C (14.1%) and 650°C (12.7%) for 12S4 and 15S5 was disappeared for thee thermogram of 18S6 as the case for the sol gel before extraction. However, no dramatic change on the sol gel's composition have been observed even after the extraction with metal ions.

3.5 Optimization for the extraction of metal ions with sol gel immobilized thiacrown ethers (batch method).

Preliminary experiment revealed that the blank sol gel is not effective in removing the metal ions. Therefore, no further investigation was carried out using the blank sol gel.

3.5.1 Effect of pH

The degree of metal ions extraction by sol gel immobilized thiacrown ether was examined by shaking in the pH range of 2 – 9. The profiles of extraction are shown in **Figure 6**.

Ag^+ was quantitatively extracted from pH 2 with the optimum extraction occurred at pH 7 for 12S4 and pH 5 for both 15S5 and 18S6 sol gel. The degree of extraction slightly decreases at pH higher than their optimum pH. Meanwhile, Hg^{2+} also exhibits the same optimum pH value as Ag^+ for all the three systems. Apart from Ag^+, the percentage extraction for all the other studied metal ions are rather low (<20%) in acidic medium (pH 2). Significant extraction of some metal ions such as Zn^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+} and Ni^{2+} are observed at higher pH (>7). In conclusion, pH 7 for 12S4 sol gel and pH 5 for both 15S5 and 18S6 sol gel was selected for subsequent extraction of Ag^{+}.

3.5.2 Effect of contact time

The time required for the extraction of metal ions is of considerable importance. The extraction was carried out by shaking mechanically the metal ions solution with the sol gel sorbent for 30 min to 4 hours at room temperature (25°C) at the respective optimum pH. The results obtained are presented in **Figure 7**.

The equilibrium time for Ag^{+} is the shortest (30 min) with over 80% of extraction for the three sol gels, followed by Hg^{2+} for 15S5 (53.60%) and 18S6 (41.04%) sol gel. This equilibrium time concurs with Yost *et al.* findings.[23] After that, the increase of contact time has no noticeable effect on the extraction of Ag^{+} and Hg^{2+}. Other metal ions are not significantly (< 20%) extracted at the first 30 min. Meanwhile, the degree of extraction for some metal ions such as Ca^{2+} was found to be increased with the increase of contact time. Therefore, 30 min of extraction time was chosen for subsequent studies in order to avoid interference from other metal ions toward Ag^{+}.

3.5.3 Effect of Sol Gel Size

Two different sizes of sol gel, namely 1mm and 5mm in diameter were used to study the sol gel size effect on the extraction efficiency. The results are summarized in **Table 4**. Generally, it was observed that the smaller sol gel (1mm) exhibits better extraction results than bigger sol gel (5mm). Therefore, 1mm size of the sol gel was adopted for subsequent experiment.

3.5.4 Reusability of sol gel

In the test of sorbent reusability, the sol gel were reused for extraction through three cycles. The results of the regeneration studies are shown in **Table 5**.

The 12S4 and 15S5 sol gel still maintain their extraction ability in the second repeated cycle of extraction and slightly decrease in the third one. No significant decrease of capacity was observed for 18S6 sol gel. The sorption capacity was reduced < 10% for 15S5 sol gel and 20% for 12S4 sol gel after 3 repeated cycles of extraction. About 61.62%, 82.14% and 91.93% of Ag^+ still can be extracted from aqueous solution after three cycles of extraction using the studied sol gels respectively. However, the amount of interferences has increased upon the reuse of the sol gel.

3.5.5 Selective preconcentration of Ag^+ in river water sample

The proposed method was used for the preconcentration and determination of Ag^+ in river water. The river waters was firstly directly analyzed with ICP-MS to determine the metal ions content. No Ag^+ was detected in the sample. Therefore, various concentration of Ag^+ (0.5, 1, 2 and 4 ppm) was spiked respectively to the samples. The results of the extraction are shown in **Figure 8**. Over 80% of 0.5 and 1 ppm spiked Ag^+ was extracted by 15S5 and 18S6 sol gel. However, as the amount of spiked Ag^+ increasess to 2 and 4 ppm, the percentage of extraction decreases drastically. This is proved that the extraction ability of the sol gel matrix is greatly affected by the capacity, which depends upon the amount of thiacrown ether immobilized into it.[32]

3.6 Optimization for off-line preconcentration of Ag^+ (column method)

Prior to the optimization, the control measurement was done on the blank column and the result shows that the column itself did not significantly retain Ag^+.

3.6.1 Effect of flow rate

The effect of different flow rates on the recovery of Ag^+ was studied by passing 10ml of 2.5ppm of Ag^+ solution at pH 5 through a column with 0.02M of 12S4, 15S5, 18S6 thiacrown ether. The flow rate was varied between 2.5 to 7.5 ml min^{-1}. It was found that the Ag^+ was quantitatively extracted for all the studied flow rates (**Figure 9**). Therefore, in subsequent experiments, a flow rate of 2.5 ml min^{-1} for retention of Ag^+ was maintained.

3.6.2 Effect of the concentration of thiacrown ether immobilized on the column

In order to obtain the quantitative recovery of Ag^+, six different concentrations of thiacrown ethers, 5×10^{-4} to 2×10^{-2} M were immobilized onto the column. Ag^+ solution at pH 5 was passed through the column at flow rate of 2.5 ml/min. The results are presented in **Figure 10**. For the 18S6 immobilized column, the degree of adsorption was hardly affected by the amount of ligand. However, the percentage extraction of Ag^+ increases gradually when the concentration of loaded 12S4 and 15S5 increases from 5×10^{-4} to 2×10^{-2} M. In conclusion, 0.02M of thiacrown ether was used for all the subsequent experiments.

3.6.3 Effect of Ag^+ concentration

The effect of Ag^+ concentration on the adsorption efficiency was tested by passing different concentration of Ag^+ from 2.5 to 10 ppm. From the results in (**Figure 11**), all the thiacrown ethers follow similar patterns of adsorption curve. A gradually decrease in the column efficiency with the increase of Ag^+ concentration was found. However, the column still performs very well (>80%) even up to 10 ppm of Ag^+.

3.6.4 Reusability of the thiacrown ether immobilized column

The reusability of the column was tested for its effectiveness to extract the metal ion (Ag^+) loading several times. In the experiment, the extraction and elution was repeated three times on the same column. The extraction ability of the thiacrown ether practically did not change after repeated use for 3 times. However, the use of new column for every sample is recommended to reduce the possibility of contamination.

3.6.5 Effect of foreign metal ions

The presence of metal ions in water may compete with Ag^+ to form complex with the trapped thiacrown ether. Therefore, the selectivity of thiacrown ether was studied by passing the aqueous solution containing 2.5ppm of metal ions mixture (Mg^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ca^{2+}, Cu^{2+}, Ni^{2+}, Ag^+, V^{4+} and Hg^{2+}) through the column under the optimum condition. According to **Figure 12**, Ag^+ was quantitatively extracted. However, its degree of extraction seems to decrease compared to the value obtained in the absence of foreign metal ions. This may be due to the presence of Hg^{2+} and Cu^{2+} which also have strong affinity toward thiacrown ether.[33] However, the percentage extraction of other studied metal ions were negligible.

3.6.6 Preconcentration and recovery of Ag^+ from real water samples

In order to assess the reliability of the proposed method, preconcentration and recovery of Ag^+ from large sample volume (1000ml) was conducted on different water samples namely, milli-Q water, tap water, rain water, river water and lake water. The results obtained are summarized in **Table 6**.

Firstly, each water sample was directly analyzed with ICP-MS to determine the metal ions content. No Ag^+ was detected in all the samples. Then 20ppb of Ag^+ was spiked to the samples. After adjusting the pH, the water was passed through the column with the flow rate of 15ml min^{-1}. Hence, 1000ml of the water sample were preconcentrated within 1 hour. After the extraction, the Ag^+ was stripped from the column with 10ml of 0.5M HNO_3. Ag^+ was significantly extracted (**Table 6**) by all the three thiacrown ethers and good recovery was achieved.

4. Conclusion

Comparison of the batch and column method

Three thiacrown ethers 12S4, 15S5 and 18S6 were immobilized into two different solid supports namely, sol gel matrix and SPE column. Results from the extraction of metal ions using the batch and column methods revealed that all the thiacrown ether exhibit high selectivity toward Ag^+. However, the extraction efficiency of 12S4 is slightly lower than the 15S5 and 18S6. This may be due to macrocyclic-ring size effect of the thiacrown ether. In addition, significant extraction was also observed for Hg^{2+} in batch method and for both

Hg^{2+}, Cu^{2+} in column method. The interference of Hg^{2+} and Cu^{2+} occurred because they are class b and ab metal ions which also have high affinity toward thiacrown ether.[34]

The equilibrium time for Ag^{+} in batch method is 30 min. Although this period of time is identical with other sol gel extraction findings[23,35], the kinetic is too slow to be implemented in column extraction. Besides, the capacity of sol gel matrix for thiacrown ethers and metal ions is lower than the SPE column. Therefore, the column method seems to be more effective as it is applicable for large sample volume at fast rate. The optimized procedures were successfully applied for the separation and preconcentration of Ag^{+} in different water samples.

Reference

1. Bradshaw, J. S. & Hui, J. Y. K. (1974) Macrocyclic sulfide synthesis: A review (1). *Journal of Heterocyclic Chemistry*. **11**, 649-673.

2. Pedersen, C. J. (1971). Macrocyclic polyether sulfides. *J. Org. Chem*. **36**, 254-257.

3. Christensen, J. J., Hill, J. O. & Izatt, R. M. (1971). Ion binding by synthetic macrocyclic compounds. Selective ion binding in the interior of ring structure characterize these compounds. *Science*. **174**, 459-467.

4. Patai, S. (1980). *Supplement E: The chemistry of ethers, crown ethers, hydroxyl groups and their sulphur analogue part (II)*. New York: John Wiley & Sons.

5. Sevdic, D,. Fekete, L. & Meider, H. (1980). Macrocyclic polythiaethers as solvent extraction reagents (III). Extraction and complex formation of silver (I) and mercury

(II) picrates. *J. Inorg. Nucl. Chem.* **42**, 885-889.

6. Saito, K., Masuda, Y. & Sekido, E. (1983). Liquid-liquid extraction of metal ions by the thiacrown compound 1,4,8,11-tetrathiacyclotetradecane. *Anal. Chim. Acta.* **151**, 447-455.

7. Sekido, E., Kawahara, H. & Tsuji, K. (1988). Liquid-liquid extraction of some class b metal ions with a thiacrown compound 1,4,7,10,13,16-hexathiacyclooctadecane. *Bull. Chem. Soc. Jpn.* **61**, 1587-1591.

8. Ikeda, K. & Abe, S. (1998). Liquid-liquid extraction of cationic metal complexes with *p*-nonylphenol solvent: Application to crown and thiacrown ether complexes of lead (II) and copper (II). *Anal. Chim. Acta*. **363**, 165-170.

9. Garg, B. S., Sharma, R. K., Bhojak, N. & Mittal, S. (1999). Chelating resins and their application in the analysis of trace metal ions. *Microchemical Journal*. **61**, 94-114.
10. Thurman, E. M. & Mills, M. S. (1998). *Solid-phase extraction. Principle and practice*. New York: John Wiley & Sons.

11. Camel, V. (2003). Solid phase extraction of trace elements. *Spectrochimica Acta Part B*. **58**, 1177-1233.

12. Bruening, R. L., Tarbet, B. J., Krakowiak, K. E, Bruening, M. L., Izatt, R. M & Bradshaw, J. S. (1991). Quantitation of cation binding by silica gel bond Thiamacrocycles and the design of highly selective concentration and purification column for palladium (II), gold (III), silver (I) and mercury (II). *Anal. Chem.* **63**, 1014-1017.

13. Goswami, A., Singh, A. K., & Venkataramani, B. (2003). 8-hydroxyquinoline anchored to silica gel via new moderate size linker: synthesis and applications as a metal ion collector for their flame atomic absorption spectrometric determination.

Talanta. **60**, 1141-1154.

14. Uzun, A., Soylak, M. & Elci, L. (2001). Preconcentration and separation with Amberlite XAD-4 resin; determination of Cu, Fe, Pb, Ni, Cd and Bi at trace levels in water samples by flame atomic absorption spectrometry. *Talanta*. **54**, 197-202.

15. Ferreira, S. L. C., Brito, C. F. D., Dautas, A. F., Araujo, N. M. L. D. & Costa, A. C. S. (1999). Nickel determination in saline matrices by ICP-MS after sorption on Amberlite XAD-2 loaded with PAN. *Talanta*. **48**, 1173-1177.

16. Narin, I., Soylak, M., Elci, L. & Dogan, M. (2000), Determination of trace metal ions by AAS in natural water samples after preconcentration of pyrocatechol violet complexes on an activated carbon column. *Talanta*. **52**, 1041-1046.

17. Hirata. S., Kajiya, T., Takano, N., Aihara, M., Honda, K., Shikino, O. & Nakayama, E. (2003). Determination of trace metals in seawater by on-line column preconcentration inductively coupled plasma mass spectrometry using metal alkoxide glass immobilized 8-quinolinol. *Anal. Chim. Acta*. **499**, 157-165.

18. Shorin, Y., Iwamoto, S., Akiyama, S., Fujita, T., Kuqli, T., Obata, H., Nakayama, E., Goda, S., Fujishima, Y., Hasegawa, H., Ueda, K. & Matsui, M. (1998). Determination of trace elements in seawater by fluorinated metal alkoxide glass-immobilized 8-hydroxyquinoline concentration and high-resolution inductively coupled plasma mass spectrometry detection. *Anal. Chim. Acta*. **363**, 11-19.

19. Bagheri, M., Mashhadizadeh, M. H. & Razee, S. (2003). Solid phase extraction of gold by sorption on octodecyl silica membrane disks modified by pentathia-15-crown-5 and determination by AAS. *Talanta*. **60**, 839-844.

20. Yamini, Y., Alizadeh, N. & Shamsipur, M. (1997). Solid phase extraction and determination of ultra amounts of mercury (II) using octadecyl silica membrane disks

modified by hexathia-18-crown-6-tetraone and cold vapour atomic absorption spectrometry. *Anal. Chim. Acta*. **335**, 69-74.

21. Moyer, B.A., Case, G. N., Alexandratos, S. D. & Kriger, A. A. (1993). Extraction of Cu (II) from sulfuric acid by macrocycle-synergized cation exchange: comparing novel impregnated resin with its solvent extraction analog. *Anal. Chem*. **65**, 3387-3395.

22. Lin, J. & Brown, C. W. (1997). Sol-gel glass as matrix for chemical and biochemical sensing. *Trends in Analytical Chemistry*. **16**, 200-211.

23. Yost, T. L., Fagan, B. C., Allain, L. R., Barnes, C. E., Dai, S., Sepanial, M. J. & Xue, Z. (2000). Crown ether-doped sol-gel materials for strontium (II) separation. *Anal. Chem*. **72**, 5516-5519.

24. Nakanishi, K. (1962). *Infrared absorption spectroscopy practical*. Nankado Company Limited.

25. Mansur, H. S., Vasconcelos, W. L., Lenza, R. F. S., Orefice, R. L., Reis, E. F. & Lobato, Z. P. Journal of non crystalline solid. (2000). Sol gel silica networks with controlled chemical properties. *Journal of non crystalline solid*. **273**, 109-115.

26. Lu, Y. K. & Yan, X. P. (2004). An imprinted organic-inorganic hybrid sorbent for selective separation of cadmium from aqueous solution. *Anal. Chem*. **76**, 453-457.

27. Rao, A. V. & KulKarni, M. M. (2002). Hydrophobic properties of TMOS / TMES-based silica aerogels. *Materials Research Bulletin*. **37**, 1667-1677.

28. Scott, R. P. W. (1993). *Silica gel and bonded phases. Their production, properties and use in LC*. John Wiley & Sons.

29. Brirnker, C. J. & Scherer, G. W. (1990). *Sol gel science. The physics and chemistry of sol gel processing*. London: Academic Press, INC.

30. Chakrabarti, k., Kim, S. M., Oh, E. O. & Whang, C. M. (2002). Thermal analysis of poly(dimethysiloxane)-modified silica xerogels. *Materials Letters*. **57**, 192-197.

31. Duval, C. (1963). *Inorganic thermogravimetric analysis*. Elsevier Publishing Company.

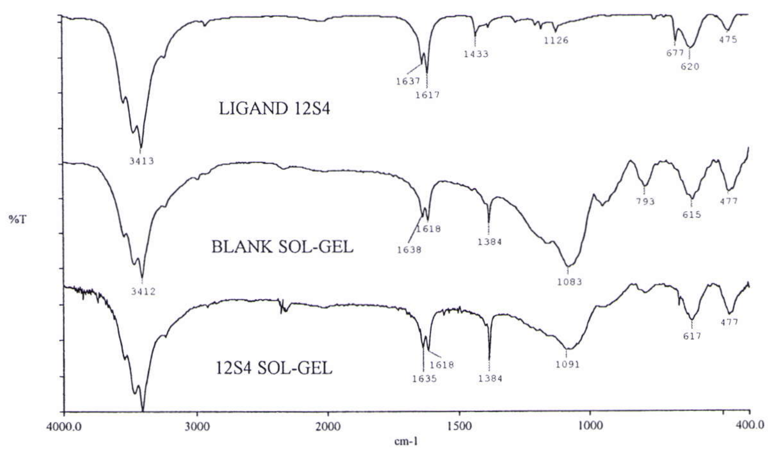
32. Duhart, A., Dozol, J. F., Rouquette, H. & Deratani, A. (2001). Selective removal of cerium from model nuclear waste solutions using a solid membrane composed of an unsymmetrical calyx[4]arenebiscrown-6 bonded to an immobilized polysiloxane backbone. *Journal of Membrane Science*. **185**, 145-155.

33. Patai, S. (1980). *Supplement E: The chemistry of ethers, crown ethers, hydroxyl groups and their sulphur analogue part (II)*. New York: John Wiley & Sons.

34. Sevdic, D. & Meider, H. (1981). Macrocyclic polythiaetherrs as solvent extraction reagents (IV). Ag(I) and Hg(II) complexes with 1,4,7,10,13,16-hexathiacyclooctadecane. *J. Inorg. Nucl. Chem*. **43**, 153-157.

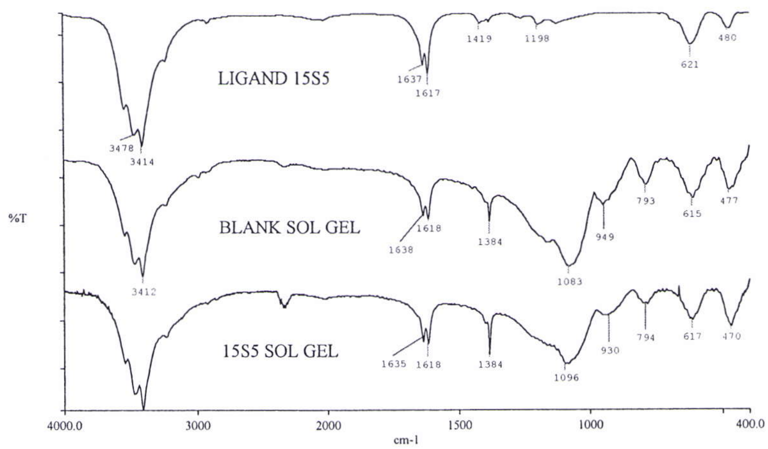
35. Seneviratne, J. & Cox, J. A. (2000). Sol-gel materials for the solid phase extraction of metals from aqueous solution. *Talanta*. **52**, 801-806.

(A)



%T
LIGAND 12S4
BLANK SOL-GEL
12S4 SOL-GEL
3413
1637
1617
1433
1126
677
620
475
3412
1618
1638
1384
1083
793
615
477
1618
1635
1384
1091
617
477
4000.0
3000
2000
1500
1000
400.0
cm-1

(B)



%T
LIGAND 15S5
BLANK SOL GEL
15S5 SOL GEL
3478
3414
1637
1617
1419
1198
621
480
3412
1618
1638
1384
1083
949
793
615
477
1635
1618
1384
1096
930
794
617
470
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3000
2000
1500
1000
400.0
cm-1

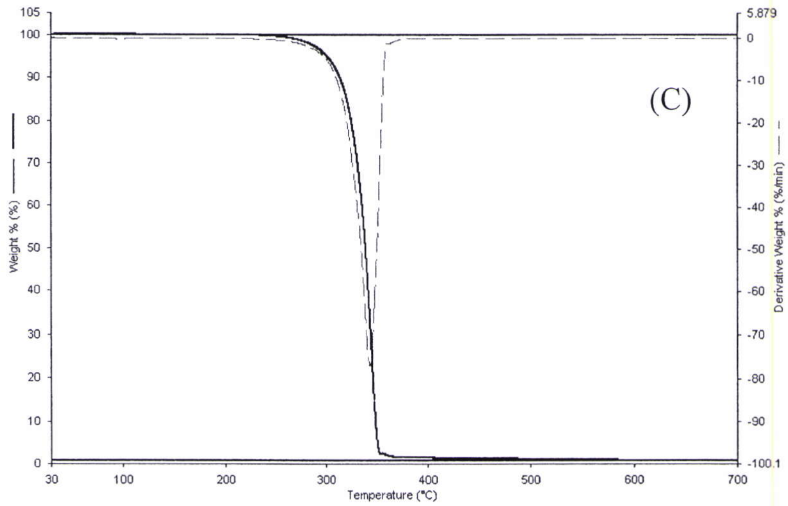


Fig 3. The thermogravimetric analysis of the free ligands. (A) 12S4, (B) 15S5 and (C) 18S6.

(C)

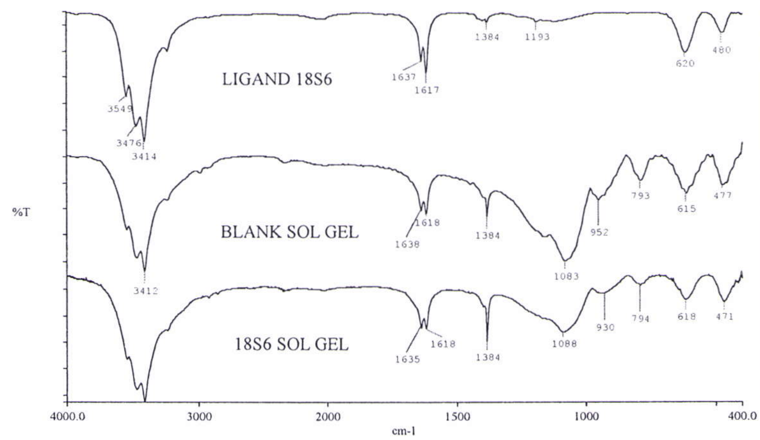
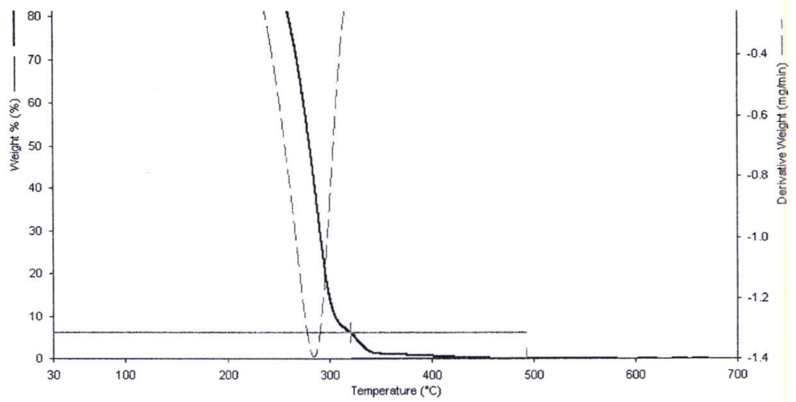


Fig 2. FTIR spectra of free thiacrown ether ligands, blank sol gel and sol gel immobilized thiacrown ether for (A) 12S4 (B) 15S5 (C) 18S6

(A)



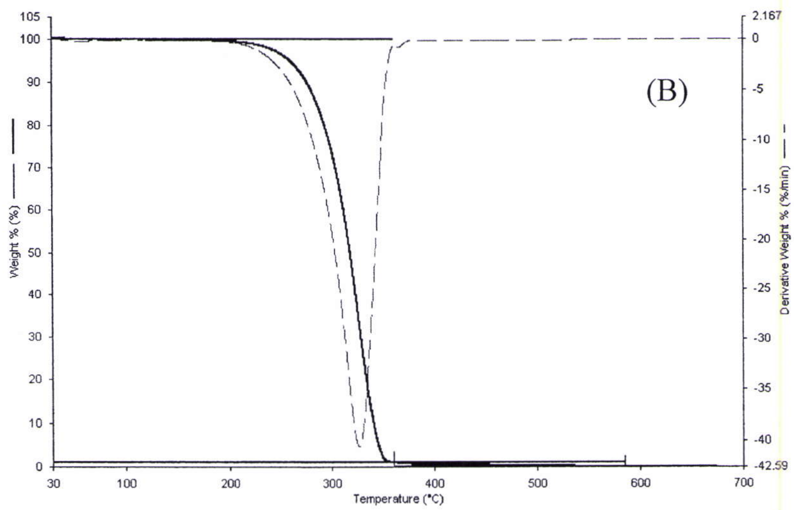


Table 3. Thermal analysis of the free thi[illegible]own ethers, blank sol gel and thiacrown et[illegible]ol gel

		Temperature range (°C)	% Loss	Decomposition temperature (°C)	Residue	Process
Free ligand	**12S4**	30-320	93.932	280	6.100	endo (s)
		320-700	6.096	-	0.0041	endo (sh)
	15S5	30-360	99.027	330	1.023	endo (s)
		360-700	1.013	-	0.0097	endo (vw)
	18S6	30-700	99.305	340	0.725	endo (s)
Sol gel	**Blank**	30-236	9.375	115	90.472	endo (wd)
		236-635	4.134	-	86.338	endo (vb)
		635-700	1.529	660	84.809	endo (s)
	12S4	30-200	10.400	115	89.555	endo (wd)
		200-460	4.845	-	84.710	endo (vb)
		460-700	6.915	468	77.795	endo (vs)
	15S5	30-203	8.873	115	90.925	endo (wd)
		203-613	4.891	-	86.035	endo (vb)
		613-700	1.423	631	84.612	endo (vs)
	18S6	30-220	9.654	-	90.173	endo (vwd)
		220-650	4.443	-	85.729	endo (vb)
		650-700	1.000	-	84.729	-
Sol gel-metal	**12S4**	30-520	14.184	-	85.609	endo (vw)
		530-572	11.094	550	74.515	endo (m)
		572-700	14.104	587	60.411	endo (m)
	15S5	30-540	12.807	-	86.909	endo (w)
		540-619	32.785	578	54.125	endo (s)
		619-700	12.724	637	41.400	endo (m)
	18S6	30-528	12.323	-	87.402	endo (b)
		528-700	15.169	562	72.233	endo (s)

b= broad, vb= very broad, m=medium, s= strong, sh= shoulder, w= week, vw= very week, wd= wide, vwd= very wide, endo= endotherrmic

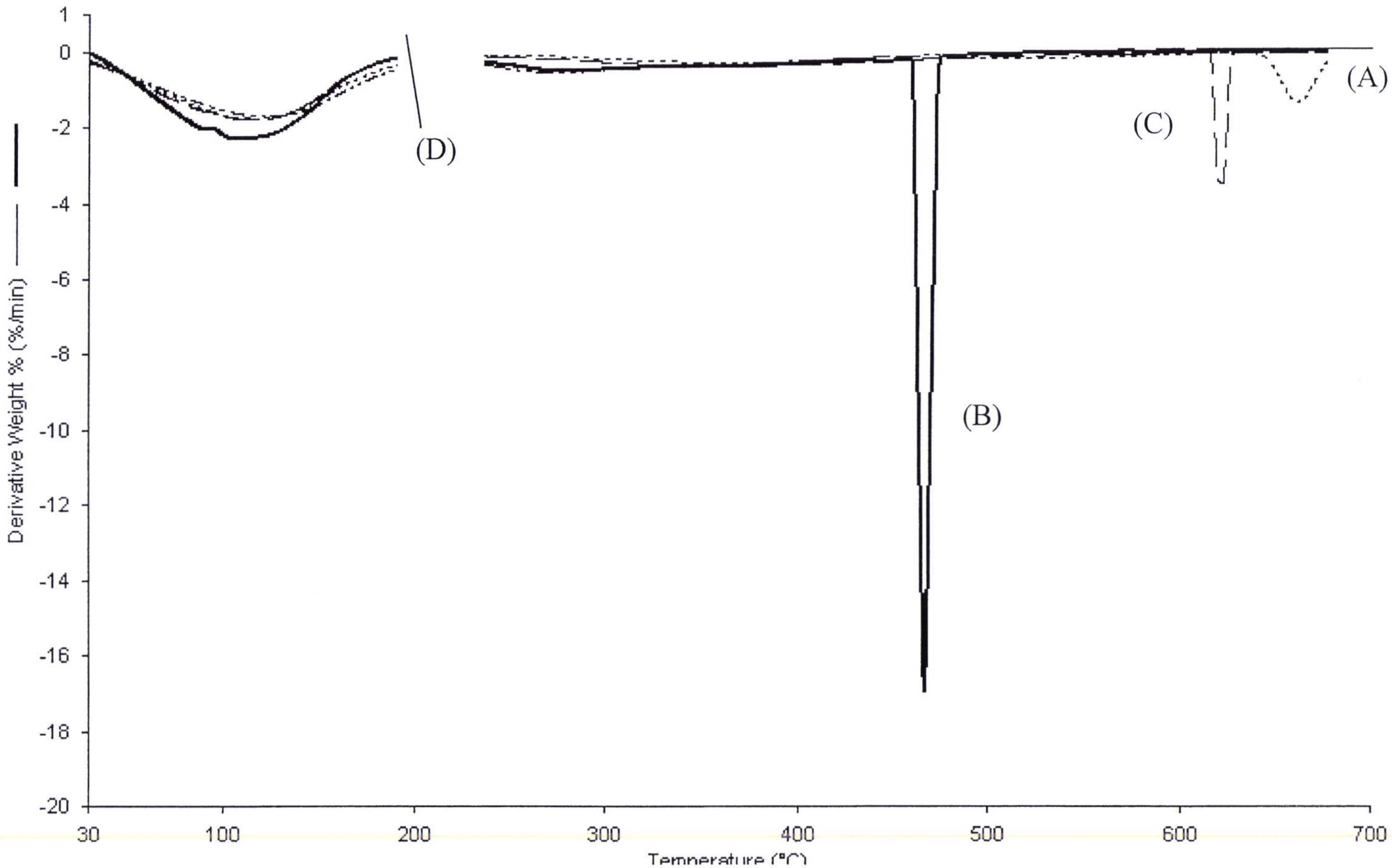


Fig 4. The thermogravimetric analysis of (A) blank (B) 12S4 (C) 15S5 (D) 18S6 sol gel

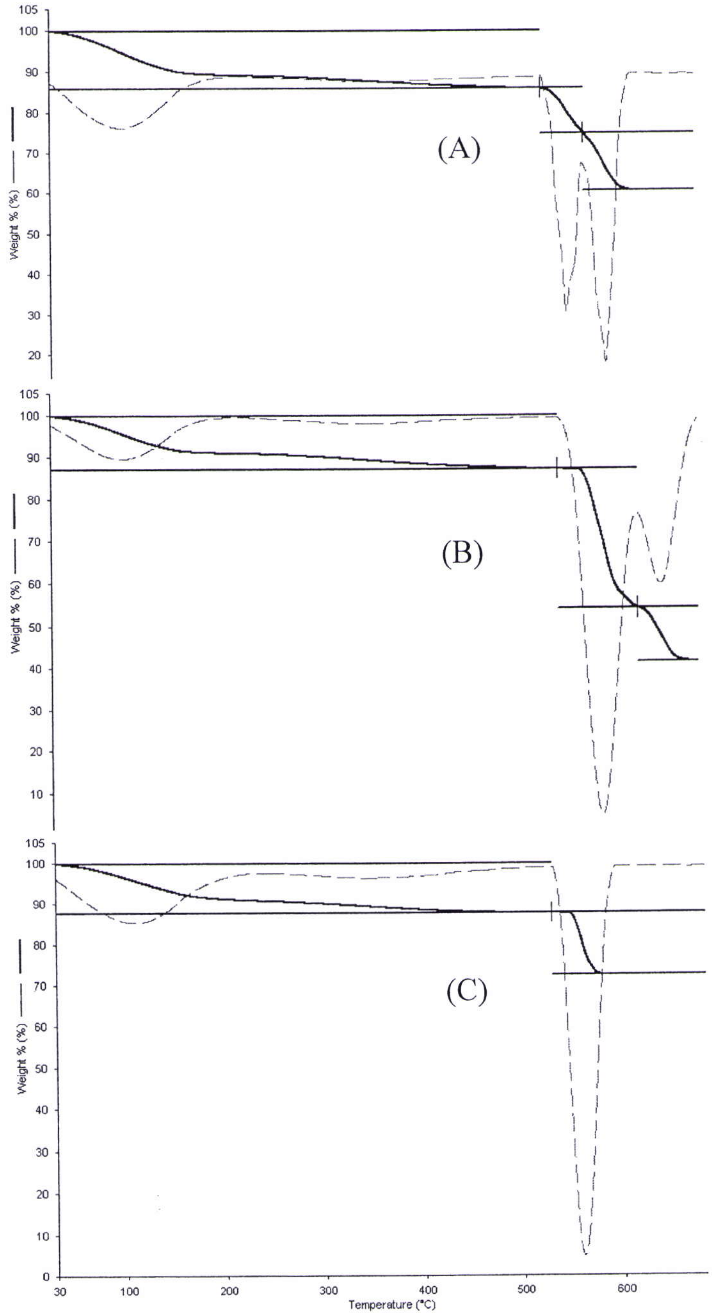


Fig 5. TGA and DTG thermogram of (A) 12S4 (B) 15S5 (C) 18S6 sol gel after shaking with metal ions solution.

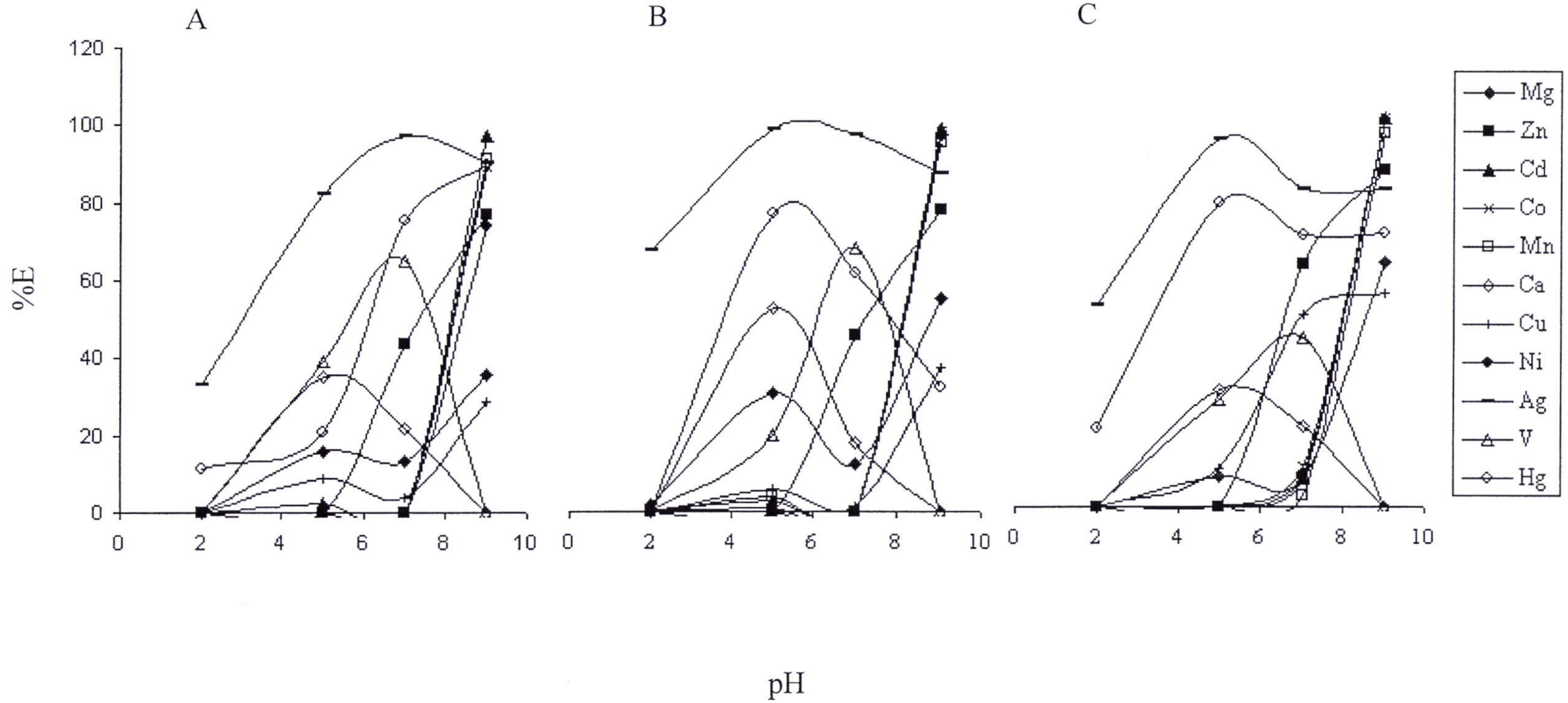


Fig 6. Effect of pH on the extraction of metal ions with sol gel immobilized thiacrown ethers (A= 12S4, b= 15S5, C= 18S6)

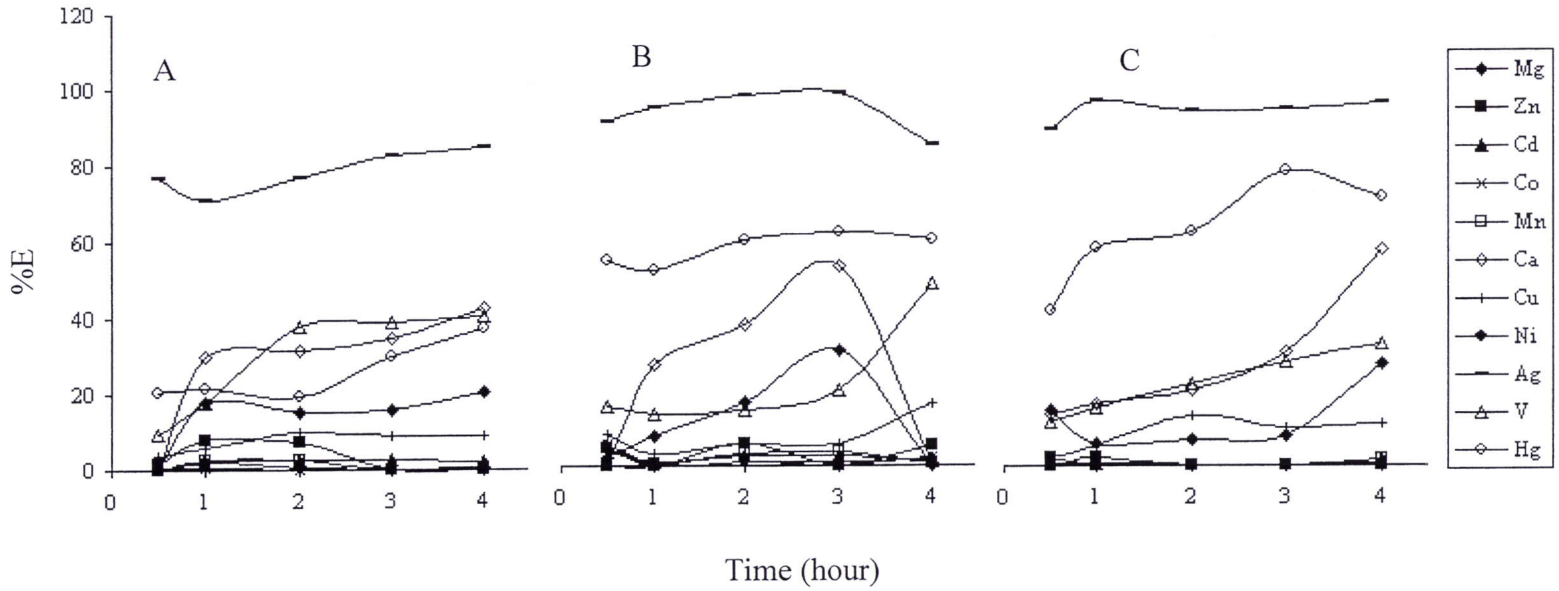


Fig 7. Effect of contact time on the extraction of metal ions with sol gel immobilized thiacrown ether (A= 12S4, B= 15S5, C= 18S6)

Table 4: Effect of sol gel size on the extraction of metal ions.

	%E					
	12S4 Sol Gel		15S5 Sol Gel		18S6 Sol Gel	
	1 mm[a]	5 mm	1 mm	5 mm	1 mm	5 mm
Mg	0	0.58	2.21	5.8	14.64	5.55
Zn	1.39	3.85	0	4.84	0	4.62
Cd	0.11	2.09	5.77	2.34	0	3.42
Co	0.11	0	5.49	0	0.84	2.26
Mn	0	0	4.83	0	2.29	3.21
Ca	0	0	0	1.86	13.43	7.87
Cu	3.50	0	8.48	0.93	2.04	1.09
Ni	0	0	4,66	0	2.20	1.57
Ag	77.05	64.91	89.77	69.86	88.57	62.99
V	9.57	0	15.51	4.31	11.39	2.63
Hg	20.30	47.86	53.60	32.02	41.04	19.59

[a] Diameter of sol gel

Table 5: Reusability sol gel through three extraction cycle.

	%E								
	12S4 Sol Gel			15S5 Sol Gel			18S6 Sol Gel		
Cycle / Metal	1	2	3	1	2	3	1	2	3
Mg	0	0	12.89	2.21	6.62	7.89	14.64	0	13.43
Zn	1.39	0	0	0	0	0	0	0	1.80
Cd	0.11	0	0	5.77	0	0	0	0	0.88
Co	0.11	0	0.75	5.49	0.38	0	0.84	0	0.64
Mn	0	0	3.19	4.83	0	0.24	2.29	0	4.19
Ca	0	0	10.13	0	40.37	8.99	13.43	0	25.18
Cu	3.50	0	0.68	8.48	21.32	7.58	2.04	6.92	6.89
Ni	0	0	0	4.66	0.08	0	2.2	0	1.34
Ag	77.05	71.72	61.62	89.77	84.66	82.14	88.57	89.35	91.93
V	9.57	12.85	21.54	15.51	44.27	42.08	11.39	0	38.30
Hg	20.30	16.40	22.92	53.60	58.40	53.19	41.04	42.80	44.24

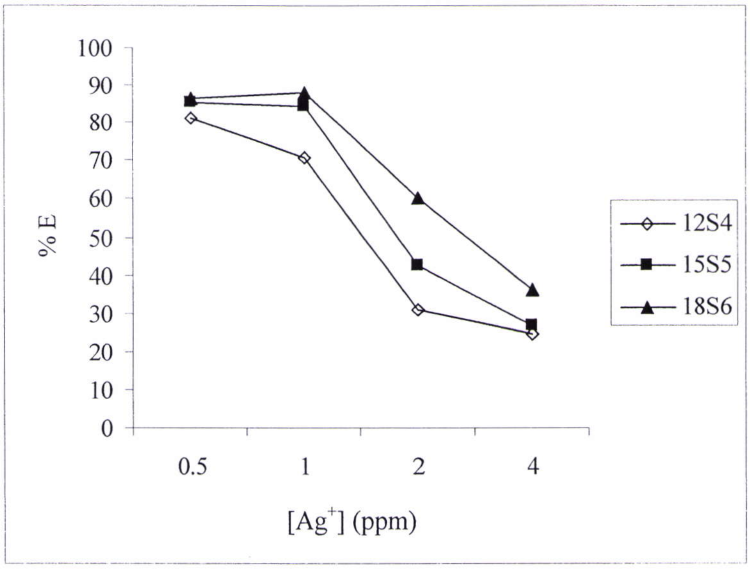


Fig 8. %E of Ag^+ from spiked river water sample with sol gel immobilized thiacrown ether

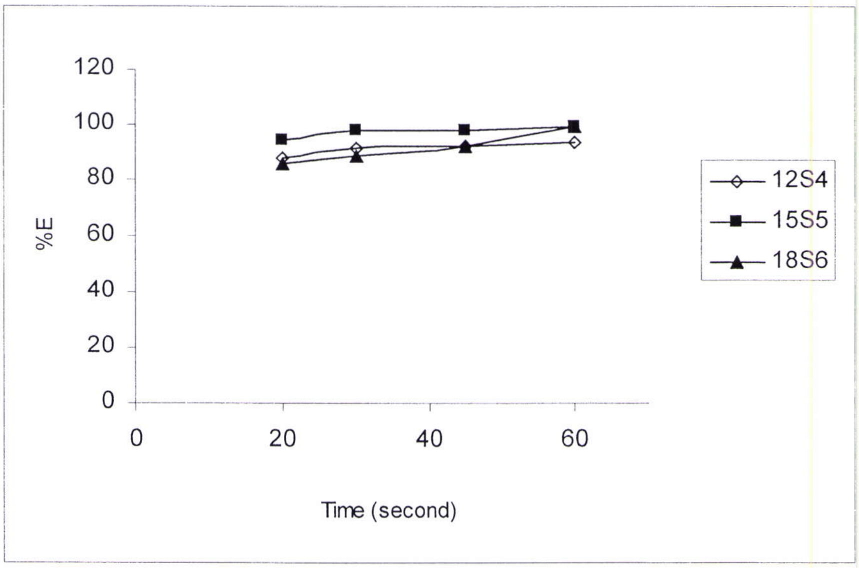


Fig 9. Effect of flow rate (2.5ml) on the extraction of Ag^{+}

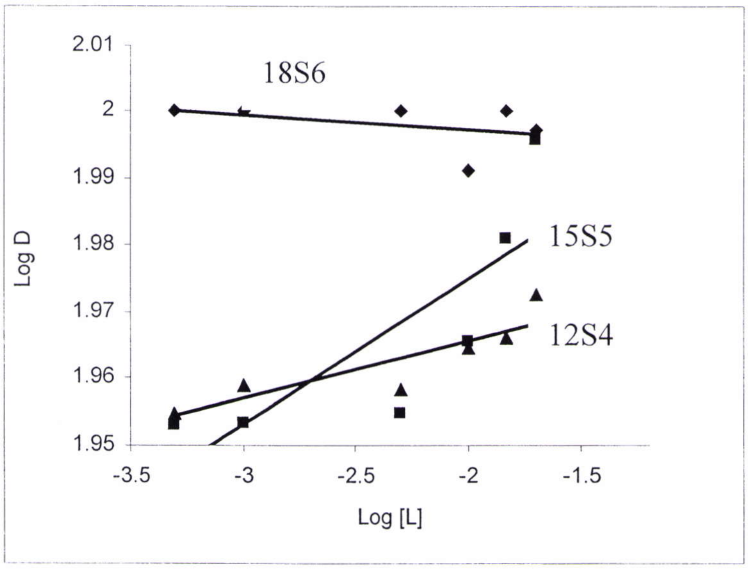


Fig 10. Effect of immobilized thiacrown ether concentration on the extraction of Ag^{+}

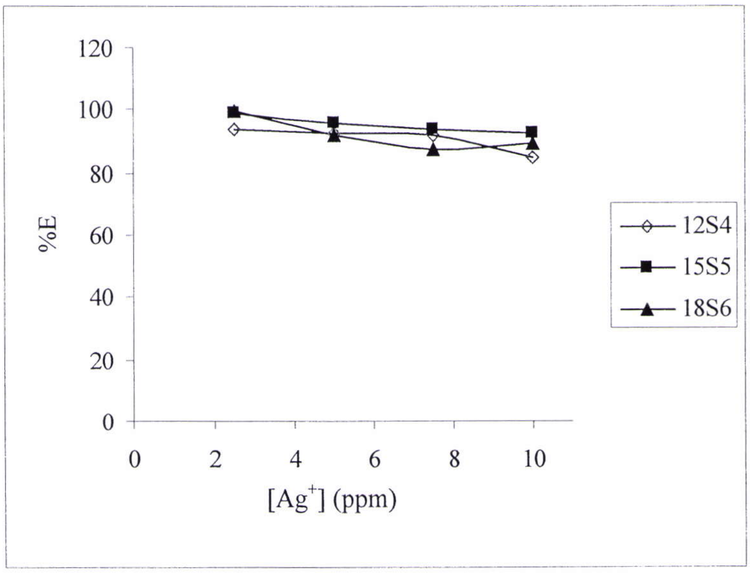


Fig 11. Effect of Ag^{+} concentration in the immobilized column efficiency

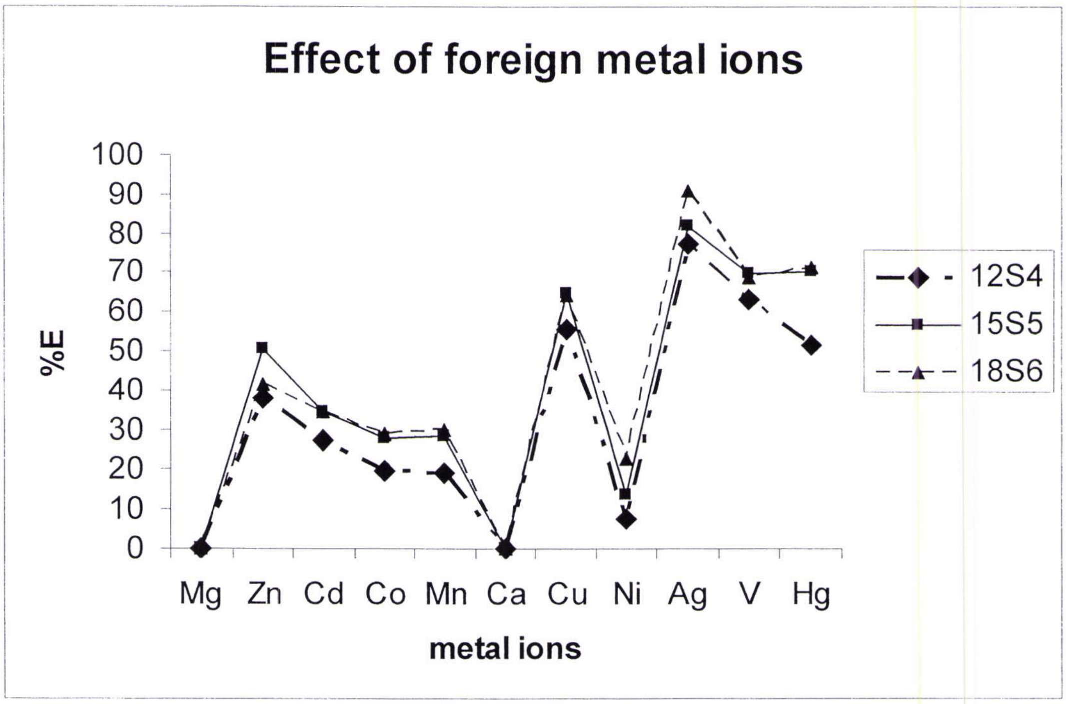


Fig 12. Effect of foreign metal ions on the extraction of Ag^+ with three thiacrown ethers immobilized sol gel.

Table 6. recovery of Ag^+ from 1000ml water samples[a]

sample	12S4		15S5		18S6	
	%E	%R	%E	%R	%E	%R
Mili-Q water	91.02 (1.6)	102.61 (5.0)	99.59 (0.4)	97.69 (5.7)	87.40 (1.6)	106.05 (0.1)
Tap water	90.57 (1.2)	105.72 (5.9)	95.45 (4.0)	101.26 (5.1)	86.48 (0.2)	98.35 (1.0)
Rain water	73.26 (1.6)	103.11 (1.0)	93.34 (1.3)	92.01 (1.0)	60.28 (3.8)	94.66 (2.7)
River water	80.92 (1.7)	109.23 (1.0)	72.92 (1.4)	103.58 (2.9)	67.76 (2.2)	88.17 (1.0)
Lake water	100 (0.1)	93.26 (2.1)	85.72 (1.7)	97.96 (1.5)	72.88 (1.1)	92.02 (0.6)

[a] Each sample contains 20ppb Ag^+

Value in paratheses are R.S.D based on three replicate analysis.

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AN IMPROVED MULTIVARIATE SHORT RUN CONTROL CHART BASED ON THE CUSUM STATISTIC

27567

[1]Michael B.C. Khoo & H.L. Gan

School of Mathematical Sciences, Universiti Sains Malaysia, 11800 Minden, Penang, MALAYSIA

[1]mkbc@usm.my

Abstract

Short run control charting is necessary at the start-up of a process and at the initiation of a new process for which prior information is unavailable. Numerous univariate short run control charts have been introduced to overcome the problems faced by conventional charts in a short run environment. Most practical scenarios involve several related variables. The multivariate short run charts for individual measurements and subgrouped data were proposed so that a joint monitoring of several correlated variables can be made simultaneously in a short run environment (see [5]). This paper aims at improving the performance of the multivariate short run chart for individual measurements by using its statistics to construct a cumulative sum (CUSUM) chart.

Keywords: short run; cumulative sum (CUSUM); Type-I error; non-centrality parameter; in-control; out-of-control (o.o.c.)

1. Introduction

Among the problems encountered by conventional charts in a short run environment is a frequent paucity of relevant data available for estimating process parameters and establishing control limits as well as the existence of many different types of measurements which require a large number of conventional charts. Research on short run charts to address these problems include the Q charts (see [6] – [10]), Zed chart (see [12]), DNOM chart (see [2]), two-stage $\overline{X}-R$ charts (see [1], [3] and [11]). The multivariate short run charts were proposed to enable a simultaneous monitoring of several correlated variables in a short run environment (see [5]). The main advantages of these charts are they allow control charting to be implemented after the first few units of production without the availability of a historical data set and enabling different variables of a process to be plotted on the same chart because all statistics are charted on a standard scale. Section 2 gives a brief discussion on the multivariate short run control chart for individual measurements.

2. Multivariate Short Run Control Chart for Individual Measurements

Let $X_n = (X_{n1}, X_{n2}, ..., X_{np})'$, $n = 1, 2, \ldots$ denotes the $p \times 1$ vector of quality characteristics, where X_{nj} is the observation on quality characteristic j at time n. It is assumed that $X_1, X_2, ...$ are independently and identically distributed (i.i.d.) vectors with a multivariate $N_p(\mu, \Sigma)$ distribution. The estimated mean vector obtained from a sequence of random vectors, $X_1, X_2, ..., X_n$ is defined as $\overline{X}_n = (\overline{X}_1, \overline{X}_2, ..., \overline{X}_p)'$ where $\overline{X}_j = \sum_{i=1}^{n} X_{ij} / n$ is the estimated mean for quality characteristic j made from the first n observations. The required notations are as follow (see Table 1):

Table 1: Notations for Cumulative Distribution Functions

$\Phi(\cdot)$	*The standard normal cumulative distribution function*
$\Phi^{-1}(\cdot)$	*The inverse of the standard normal cumulative distribution function*
$H_v(\cdot)$	*The chi-squared cumulative distribution function with v degrees of freedom*
$F_{v_1,v_2}(\cdot)$	*The Snedecor-F cumulative distribution function with (v_1, v_2) degrees of freedom*

The following formulas give the V statistics of the multivariate short run chart for the two cases of both μ and Σ known and unknown (see [5]):

Case KK: $\mu = \mu_0$, $\Sigma = \Sigma_0$, *both known*

$$T_n^2 = (X_n - \mu_0)' \Sigma_0^{-1} (X_n - \mu_0)$$

and

$$V_n = \Phi^{-1}\{H_p(T_n^2)\}, \quad n = 1, 2, \ldots \tag{1}$$

Case UU: μ and Σ both unknown

$$T_n^2 = (X_n - \overline{X}_{n-1})' S_{n-1}^{-1} (X_n - \overline{X}_{n-1})$$

where

$$S_n = \frac{1}{n-1} \sum_{i=1}^{n} (X_i - \overline{X}_n)(X_i - \overline{X}_n)'$$

and

$$V_n = \Phi^{-1}\left\{F_{p,n-p-1}\left[\left(\frac{(n-1)(n-p-1)}{np(n-2)}\right)T_n^2\right]\right\}, \quad n = p+2, p+3, \ldots \tag{2}$$

Note that p (see Eqs. 1 and 2) is the number of quality characteristics monitored simultaneously, hence $p \geq 2$, while S_n is the unbiased estimator of Σ. The V statistics in Eqs. 1 and 2 are all i.i.d. $N(0,1)$ variables (see [5]).

3. An Improved Short Run Multivariate Control Chart

Since from the previous section the V_n statistics in eqs. (1) and (2) are all i.i.d. $N(0,1)$ random variables, a cumulative sum (CUSUM) chart can be constructed from the sequence of the V statistics to enhance the performance of the short run multivariate chart because the CUSUM is a memory control chart. The following equation gives the upper-sided (C^+) CUSUM statistic (see [7]):

$$C_i^+ = \max\{0, C_{i-1}^+ + V_i - k_s\}, \quad i = 1, 2, \ldots \tag{3}$$

The starting value is $C_0^+ = 0$ while the reference value, k_s and decision interval, h_s are selected based on a desired Type-I error. Note that only the upper-sided CUSUM statistic (Eq. 3) is considered because the short run multivariate chart is directionally invariant (see [5]), i.e. its performance depends only on the magnitude of a shift in the mean vector given by the square root of the non-centrality parameter (Eq. 4) and not in the direction of the shift.

$$\lambda^2 = (\mu_s - \mu_0)' \Sigma_0^{-1} (\mu_s - \mu_0) \tag{4}$$

Here, μ_0 and μ_s represent the in-control and out-of-control mean vectors respectively while Σ_0 denotes the covariance matrix.

4. An Evaluation of the Performance of the Improved Chart

A simulation study using SAS version 8 is conducted to study the performance of the improved chart based on the CUSUM statistic for a bivariate case where the number of quality characteristics, $p = 2$. An in-control process is assumed to follow a bivariate normal $N_2(\mu_0, \Sigma_0)$ distribution where $\mu_0 = (0,0)'$ and $\Sigma_0 = \begin{pmatrix} 1 & \rho \\ \rho & 1 \end{pmatrix}$. A shift in the mean vector from μ_0 to μ_s for the following three cases are considered:

Case 1: $\mu_s = (\delta,0)', (0,\delta)', (-\delta,0)'$ or $(0,-\delta)'$

Case 2: $\mu_s = (\delta,\delta)'$ or $(-\delta,-\delta)'$

Case 3: $\mu_s = (\delta,-\delta)'$ or $(-\delta,\delta)'$

Note that all of the above o.o.c. mean vectors, μ_s, for the same case are of the same distance away from the in-control mean vector, μ_0 (see [5]). Since the improved chart and its basic counterpart are directionally invariant, only the first μ_s for each of the above cases will be considered. Correlation coefficients of $\rho = 0$, 0.2, 0.5 and 0.8 are considered.

For each value of $c \in \{10, 20, 50\}$, c in-control observations are generated from a $N_2(\mu_0, \Sigma_0)$ distribution followed by 30 o.o.c. observations from a $N_2(\mu_s, \Sigma_0)$ distribution. This is repeated 5000 times and the proportion of times an o.o.c. signal is observed from c+1 to c+30 for the first time is recorded.

Because of space constraint, only the results of $\mu_s = (\delta, 0)'$ and ρ = 0.5 are given (see Table 2). The results for the other cases also have similar trend. The results are given for the 1-of-1, 3-of-3, 4-of-5, EWMA (see [4]) and the CUSUM tests. Note that the results of the improved chart denoted by CUSUM (see Table 2) are obtained from a simulation study using Eq. 3 with k_s = 0.75 and h_s = 3.34 where these two values are chosen to obtain a Type-I error similar to that of the 1-of-1 test. Given a sequence of V statistics, $V_a, V_{a+2}, \ldots, V_m$, $a \geq 0$, the 1-of-1, 3-of-3, 4-of-5 and EWMA tests are defined as follow (see [5]):

The 1-of-1 test: When V_m is plotted, the test signals a shift in μ if $V_m > 3$.

The 3-of-3 test: When V_m is plotted, the test signals a shift in μ if V_m, V_{m-1} and V_{m-2} all exceed 1.

The 4-of-5 test: When V_m is plotted, the test signals a shift in μ if at least four of the five values $V_m, V_{m-1}, \ldots, V_{m-4}$ exceed 1.

The EWMA test: The EWMA statistic Z_m is defined as $Z_m = \alpha V_m + (1-\alpha) Z_{m-1}$, m=b, b+1,.. where $b \geq 1$ and $Z_{b-1} = 0$. The EWMA chart is constructed based on $UCL = K\sqrt{\alpha/(2-\alpha)}$ where the values of (α, K) used are (0.25, 2.90) which gives UCL=1.096. These values are chosen to give an in-control average run length (ARL) of 3726 and an ARL of 5.18 to detect a shift of 1.5 standard deviations in a normal mean (see [5]). An o.o.c. signal is given at time m if $Z_m > 1.096$.

The results show that Case KK has a superior performance to Case UU. For example, for c=10 and δ=1, the o.o.c. proportions of Case KK for the 1-of-1, 3-of-3, 4-of-5, EWMA and CUSUM tests are 0.319, 0.583, 0.506, 0.673 and 0.628 respectively while the corresponding values of Case UU are 0.042, 0.115, 0.068, 0.050 and 0.080 respectively, where the values of Case KK are always greater than that of Case UU. Note also that for Case UU with δ>0, the o.o.c. proportion increases as the value of c increases. For Case KK, the performance of the CUSUM test is comparable to that of the EWMA test. However, the CUSUM test outperforms that of the EWMA for Case UU. The CUSUM test for Case UU has the best performance for moderate and large values of δ. Although for small values of δ>0 the 3-of-3 test seems to outperform the other tests, its false alarm rate is somewhat too high for the case of δ=0. Overall, the CUSUM test gives a good performance as it has the lowest rate of false alarm (similar to the 1-of-1 and EWMA tests) and the highest rate of detecting an o.o.c. signal for moderate and large values of δ for Case UU. If the 3-of-3 test is excluded in the comparison because of its high and unacceptable false alarm rate, then the CUSUM test performs best for Case UU even for small values of δ>0. The above discussion shows that the improved short run multivariate chart based on the CUSUM statistic has provided superior results to its standard counterpart.

5. Conclusion

We have shown in this paper that the improved short run multivariate chart outperforms its standard counterpart which makes it a good alternative to the existing approach. The new approach addresses the need for a quicker detection of o.o.c. signals in a short run environment. Further research can be made to enable process monitoring to be carried out using data from skewed and non-normal distributions.

References

1. M.E. Elam and K.E. Case, "A Computer Program to Calculate Two-Stage Short-Run Control Chart Factors for $(\overline{X}, R)$ Charts", *Quality Engineering*. **14** (2001), 77-102.
2. N.R. Farnum, "Control Charts for Short Runs: Nonconstant Process and Measurement Error", *Journal of Quality Technology*. **24** (1992), 138-144.
3. F.S. Hillier, "$\overline{X}$ Chart Control Limits based on a Small Number of Subgroups", *Industrial Quality Control*. **20** (1964), 24-29.
4. Michael B.C. Khoo, "Construction of Multivariate Control Charts and Q Chart Extensions for Short Runs Production", (Ph.D. Thesis, University Science of Malaysia, 2001).
5. Michael B.C. Khoo and S.H. Quah, "Proposed Short Runs Multivariate Control Charts for the Process Mean", *Quality Engineering*. **14** (2002), 603-621.
6. C.P. Quesenberry, "SPC Q Charts for Start-Up Processes and Short or Long Runs", *Journal of Quality Technology*. **23** (1991), 213-224.
7. C.P. Quesenberry, "On Properties of Q Charts for Variables", *Journal of Quality Technology*. **27** (1995a), 184-203.
8. C.P. Quesenberry, "On Properties of Binomial Q Charts for Attributes", *Journal of Quality Technology*. **27** (1995b), 204-213.
9. C.P. Quesenberry, "On Properties of Poisson Q Charts for Attributes", *Journal of Quality Technology*. **27** (1995c), 293-303.
10. C.P. Quesenberry, "Geometric Q Charts for High Quality Processes", *Journal of Quality Technology*. **27** (1995d), 304-315.
11. T. Pyzdek, "Process Control for Short and Small Runs", *Quality Progress*. **26** (1993), 51-60.
12. D.J. Wheeler, *Short Run SPC*. Knoxville, Tennessee : SPC Press, Inc.

		c=10					c=20					c=50				
	Case	1-of-1	3-of-3	4-of-5	EWMA	—	1-of-1	3-of-3	4-of-5	EWMA	—	1-of-1	3-of-3	4-of-5	EWMA	—
0.0	KK	0.038	0.095	0.055	0.042	0.037	0.038	0.100	0.055	0.043	0.038	0.038	0.102	0.055	0.039	0.034
	UU	0.040	0.103	0.052	0.039	0.037	0.039	0.100	0.049	0.041	0.038	0.038	0.101	0.050	0.043	0.043
0.5	KK	0.091	0.196	0.127	0.131	0.125	0.094	0.196	0.126	0.133	0.124	0.092	0.196	0.123	0.138	0.122
	UU	0.042	0.102	0.055	0.041	0.046	0.041	0.115	0.063	0.049	0.066	0.054	0.144	0.079	0.079	0.093
1.0	KK	0.319	0.583	0.506	0.673	0.628	0.311	0.583	0.500	0.669	0.627	0.315	0.583	0.499	0.670	0.623
	UU	0.042	0.115	0.068	0.050	0.080	0.056	0.165	0.098	0.097	0.158	0.098	0.281	0.197	0.217	0.311
1.5	KK	0.740	0.952	0.945	0.995	0.992	0.742	0.949	0.940	0.994	0.992	0.742	0.944	0.942	0.994	0.992
	UU	0.047	0.139	0.087	0.077	0.125	0.079	0.266	0.181	0.199	0.337	0.181	0.527	0.440	0.553	0.723
2.0	KK	0.980	1.000	0.999	1.000	1.000	0.982	1.000	1.000	1.000	1.000	0.981	1.000	1.000	1.000	1.000
	UU	0.062	0.182	0.119	0.121	0.209	0.126	0.416	0.325	0.364	0.607	0.314	0.785	0.744	0.870	0.967
2.5	KK	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	UU	0.091	0.250	0.167	0.173	0.318	0.218	0.578	0.495	0.564	0.853	0.508	0.927	0.922	0.983	1.000
3.0	KK	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	UU	0.139	0.317	0.217	0.229	0.453	0.341	0.717	0.645	0.733	0.966	0.719	0.979	0.983	0.999	1.000
4.0	KK	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	UU	0.293	0.424	0.288	0.354	0.708	0.678	0.883	0.921	0.935	1.000	0.965	1.000	1.000	1.000	1.000
5.0	KK	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	UU	0.518	0.489	0.325	0.473	0.869	0.909	0.949	0.911	0.989	1.000	0.999	1.000	1.000	1.000	1.000

Table 2: Simulation Results for the Basic and Improved Short

APPLICATION OF DESIGN OF EXPERIMENT IN PRINTED CUIRCUIT BOARD ASSEMBLY INDUSTRY

27368

V. Mathaeswari[1], U. Safian[2], & A. Zalila[3]

[1]*Celestica Malaysia Sdn. Bhd, Kulim, Kedah,Malaysia*
[2,3]*School of Mathematical Sciences, Universiti Sains Malaysia, 11800 Minden Malaysia*
[1]mlingam@celestica.com; [2]safian@cs.usm.my; [3]zalila@cs.usm.my

Abstract

Printed circuit board assembly (PCBA) is a process of mounting and inserting components to printed circuit board (PCB) by means of several principle processes such as Manual Insertion, Auto Insertion (Axial & Radial), Wave Soldering, Surface Mount Technology and Box Build. Manufacturers of PCBA are forced to produce better quality with less cost in order to stay in the business as globalization taking shape. To achieve such a goal, manufacturers are forced to strive to attain and maintain high first pass-yield. Hence, Design of Experiments (DOE) is one of the statistical tools that can be used by the manufacturers of PCBA to purposefully evaluate and optimize designs and processes; so that the manufacturers can achieve greater first pass yield and lower wastage which attributes to decrease the product cost. A project was implemented in a PCBA manufacturing company using the Full Factorial Design with two levels for the wave soldering process with the aid of MINITAB Software. And the objectives of the experiment are to determine the key factors of the process and optimize the process for higher yield. The results of the experiments were excellent, the yield at the wave soldering increased from 90.6 to 97.4. At the same time the key factors were identified and monitored closely to minimize variations.

Keywords: printed circuit board, full factorial design, wave soldering;

1. Introduction

Design of Experiments (DOE) is the statistical methodology of planning investigations and research, collecting data and data analysis. DOE identifies the key inputs or factors of a process and these factors are consciously changed to observe the consequences or outputs. A process is series of activities that convert inputs such as man, material, machine, method, etc. into the desired stage or outputs .

The main reasons for implementing DOE are to: understand and reduce variability, determine optimum operating conditions or setting, perform a comparative study, ascertain

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MODELLING THE AIDS EPIDEMIC IN MALAYSIA

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Ong Hong Choon
School of Mathematical Sciences, University of Sciences of Malaysia, 11800 USM Penang. Malaysia.
hcong@cs.usm.my

Abstract

There are generally three methods of modelling the acquired immuno deficiency syndrome (AIDS) epidemic. At one extreme is the attempt to fit a function of calendar time such as a polynomial or other mathematically convenient curves to the AIDS incidence curve while the other extreme attempts to model the full dynamics of the transmission of the epidemic in the population providing much insight into the qualitative evolution of the epidemic and identifying the key variables that detemine the future number of cases.

The method of backcalculation which is intermediate between the first two methods, estimates the past HIV infection rate from the AIDS incidence data and an estimate of the incubation period distribution. This method is used on the Malaysian data to model the AIDS epidemic because it makes use of the Malaysian AIDS incidence which is fairly reliable and is more reflective of the trend of the epidemic as compared to the HIV infection rate recorded. An application is made in this study on the AIDS incidence data in Malaysia released by the Ministry of Health, Malaysia using a backcalculation program and an approximate incubation period distribution to generate the current HIV infection rate for Malaysia.

Keywords: Backcalculation, AIDS modeling, HIV infection

1. Introtuction

Methods fo predicting the future trends in the incidence of AIDS are based on one of three methods. These methods are similar in that they all fit some function of calendar time to the incidence of AIDS data but they differ in the degree to which the mechanisms that generate the data are incorporated into the model.

At one extrene, the method fits a function of calendar time such as a polynomial or other mathematically convenient curves to the AIDS incidence curve and then extrapolates into the future (see [10]). Although this method is easily implemented, it has the danger of extrapolating a fitted model outside the range of the observed data. The prevalence of HIV infection cannot be estimated with this approach. This method ignores what is known about the epidemiology of the disease and it cannot incorporate information that one might have on changing patterns of transmission.

The second method models the full dynamics of transmission of the epidemic in the population providing much insight into the qualitative evolution of the epidemic and identifying the key variables that determine the short and medium term forecast of the number of cases (see [2]). Unfortunately, the deterministic models proposed for general epidemics are complicated, and the stochastic models are even more complicated.

Furthermore, predictions based on such models are particularly sensitive to unknown parameters such as the long incubation distribution from infection to the development of AIDS, the frequency and pattern of sexual activity and behavioural changes which change with time and also the proportion of infected people who eventually develop AIDS with allowance for emigration, immigration and death. Such models are complicated and contained many unknown parameters (see [11]).

The third approach, to be explained in this study, which is intermediate between these two approaches, is the back projection method. (see [3, 4, 9]). Backcalculation is a method of estimating past HIV infection rates from the AIDS incidence data, and an estimate of the incubation period distribution. The method requires reliable counts of the number of AIDS cases diagnosed over time and a reliable estimate of the incubation period distribution. The method is popular because it makes use of the AIDS incidence data which represent the most readily available information on the AIDS epidemic as most national AIDS surveillance data systems record only AIDS cases. The incubation period distribution is then applied to the estimated past HIV infection rates to project future AIDS incidence.

2. The Method of Backcalculation

The basic convolution equation in backcalculation relates the number of new cases of AIDS in time t to $t + dt$ (designated $Z(t)$) and the number of new HIV infections $g(s)$ at each time s since the start of the epidemic $(s = 0)$ through the incubation period distribution $f(u)$, where u is the time spent between the initial infection and the eventual diagnosis of AIDS. The basic convolution equation is given as:

$$Z(t) = \int_0^t g(s) f(t-s) ds, \tag{1}$$

From the above equation, for an individual to be diagnosed as an AIDS case by calendar time t, he or she must have been infected at some prior time s, and then have an incubation period less than $t - s$. In other words, the backcalculation method uses the above equation together with knowledge of $Z(t)$ (obtained from the AIDS cases registries) and $f(t)$ (obtained from the epidemiological studies) to give information on past infection rates $g(s)$. If $f(t)$ is known, the above relationship could be inverted to express $g(s)$ for all $0 \le s \le t$ as a function of $Z(t)$. In general, a family of values for $g(s)$, $0 \le s \le t$ can be constructed which are consistent with a realization of $Z(s)$, $0 \le s \le t$.

Let $z_1, z_2, \ldots, z_n$ be the number of AIDS cases diagnosed in the calendar time interval $[t_{i-1}, t_i)$, $i = 1, 2, \ldots, n$. It is assumed that individuals become infected according to a point process. Then the expected number of AIDS cases occurring during the time interval $[t_{i-1}, t_i)$ is given by [7, p.198]

$$E(z_i) = \int_{t_0}^{t_i} g(s).\{F(t_i - s) - F(t_{i-1} - s\}ds \qquad (2)$$

where $F(t)$ is defined to be 0 for $t \leq 0$. By convention, we shall define calendar time 0 to be the start of the epidemic (that is $g(s)$ = 0 prior to that time) and thus $t_0 = 0$.

The method of backcalculation is used because it makes use of the AIDS incidence data which is more reflective of the trend of the epidemic. The number of HIV+ cases, on the other hand, is dependent on the test made and is unreliable as a trend. For example, a steep rise in the number of HIV+ cases may be due to the mandatory testing of all intravenous drug users in drug rehabilitation centres and increase in detection through aggressive case finding.

3. Result of the Backcalculation Method on the Malaysian Data

The definitive diagnostic method for diseases indicative of AIDS used in Malaysia is taken from the Ministry of Health's publication "*Plan of Action for Prevention and Control of AIDS*" released in May 1988. This definition is similar to the CDC's 1987 definition and the WHOdefinition and has been in used in Malaysia since 1988. The under reporting rate is assumed to be 10% (around 90% reported) throughout and the reporting delay, which is around 2 to 4 weeks, from the various districts to the AIDS section, Ministry of Health is assumed to be negligible.

The backcalculation method is applied by [13] on the Malaysian data until August 1996 and obtained the estimated number of cumulative HIV infection as shown in Figure 1.

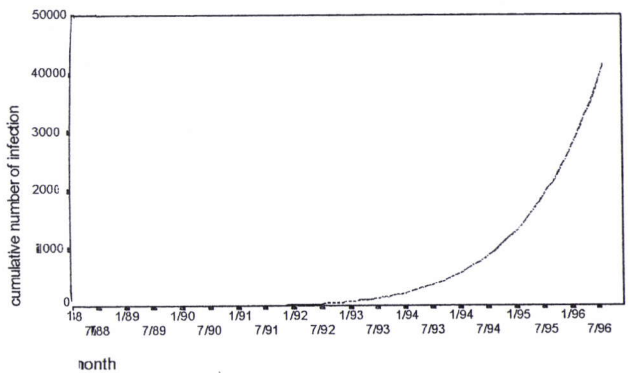

Figure 1 Estimated cumulative number of HIV infection applied to the Malaysian data till August 1996 (see [13])

An obvious result from Figure 1 is that the HIV/AIDS epidemic in Malaysia is in their early stage which is evident in its rapid exponential increase in the number of infected cases until August 1996. A backcalculation program in Fortran from [3] is used again on the Malaysian data in this paper. The program is based on the incubation period distribution from [4]. The basis for using the incubation period distribution from [4], which is based mainly on homosexuals, on the Malaysian data which are mainly intravenous drug users is because the incubation period distribution of the two cohorts are similar (see[12]).

Table 1: Cumulative HIV+ and AIDS cases recorded from the Ministry of Health, Malaysia (see [1]) and the corresponding estimated cumulative HIV+ cases from the backcalculation method in this study.

Year	Cumulative HIV+ cases recorded	AIDS Cases reported	Estimated cumulative HIV+ Cases
1986	3	1	1.62
1987	5	0	402.26
1988	14	2	1036.68
1989	214	2	1828.84
1990	992	18	2897.21
1991	2786	60	4502.37
1992	5298	73	7208.14
1993	7805	71	12064.01
1994	11198	105	20214.95
1995	15396	233	30897.54
1996	19993	347	40536.07
1997	23917	568	46741.35
1998	28541	875	50055.38
1999	33233	1200	51718.45
2000	38340	1168	52542.59
2001	44278	1302	52950.32
2002	51256	1193	53152.01

There is a slowdown in the increase of the number of estimated infected HIV+ cases in the late 1990s as can be seen from Figure 2. This trend is supported by a slowdown in the increase of the number of AIDS cases (as can be seen in Table 1) which gives a clear picture of the trend of the epidemic. Also, there is a narrowing of the gap between the number of recorded cumulative and estimated HIV+ cases. This is probably due to an increasing awareness among the population (especially the high risk group) towards the epidemic and also due the efforts by the Malaysian government and non-government organizations to promote this awareness. This slowdown in the increase is also similar to the trend in developed countries like the US and UK where the AIDS epidemic had begun earlier. (see [3, 8])

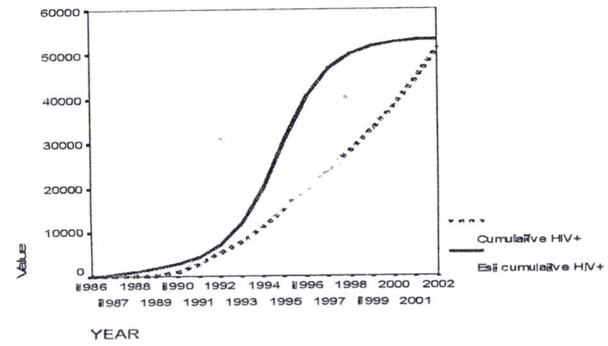

Figure 2. A comparison between the recorded and estimated cumulative number of HIV infections in Malaysia

Beside the uncertainty resulting from inaccurate knowledge of the inputs of AIDS data, the estimates from the method of backcalculation have some inherent stochastic uncertainty. The confidence bounds in Table 2 reflect only the uncertainty that would be present if we actually know the incubation and reporting inputs and the smoothness weights.

Table 2: Point wise 95% lower and upper confidence bounds of the estimated HIV+ incidences.

Year	Cumulative HIV+ estimated	Lower bound	Upper bound
1986	1.62	0	23.71
1987	402.26	229.72	574.79
1988	1036.68	789.61	1281.75
1989	1828.84	1590.70	2066.98
1990	2897.21	2590.98	3203.44
1991	4502.37	4000.09	5004.66
1992	7208.14	6478.84	7937.44
1993	12064.01	11082.89	13045.12
1994	20214.95	18796.78	21633.12
1995	30897.54	28951.01	32844.07
1996	40536.07	38096.14	42976.00
1997	46741.35	43744.66	49748.03
1998	50055.38	46405.93	53704.83
1999	51718.45	47428.19	56008.72
2000	52542.59	47705.98	57379.20
2001	52950.32	47705.65	58194.98
2002	53152.01	47630.46	58673.56

4. Discussion

There are several potential sources of error and limitations underlying the assumption of the methodology. Firstly, the parametric model for the HIV infection rate provide no information about future incidence rate as it only attempts to estimate the historical infection rates. It is for this reason that backcalculation is referred to as a method for estimating the minimum size of the epidemic (see [6]). Secondly, there is little information about the recent infection rate because of the long incubation period. However, short term projections of AIDS are reliable because such projections depend more strongly on the infection rate in the distant past than the recent ones. The third limitation is that the incubation distribution, F, is not known precisely although it is assumed known. The incubation distribution may be different for different subgroups of infected individuals with age as a cofactor of disease progression. Fourthly, the assumption of dependence between the calendar date of infection and incubation period implicit in the convolution equation would be violated if cofactors of disease progression are identified that are more prevalent among those infected earlier (or later) in calendar time. Also, a smaller f needs to be compensated by a larger g in order to fit the cumulative AIDS incidence series. The fifth potential source of limitation is in the inaccuracies in the AIDS incidence data over time. It could be clouded with issues like reporting delays and changes in AIDS definition, discussed in the previous section.

The application of backcalculation to data is useful in several aspects. Firstly, the backcalculation method provides a simple conceptual framework for relating the incubation distribution with the AIDS incidence data and the infection rate. Secondly, backcalculation leads to short-term projections of AIDS incidence that are robust to changes in the incubation distribution (see [5, 6, 14]). Thirdly, although backcalculation estimates of cumulative infections are known to be highly sensitive to the choice of f, plausible ranges of estimates of g from backcalculation for the number infected in the United States based on data through mid-1987 were in broad agreement with estimates based on surveys in selected populations (see [6, 14]).

References

1. http://dph.gov.my/aids/. Accessed on March 3, 2005.
2. M.Arca, C.A. Perucci and T. Spadea, "The epidemic dynamics of HIV-1 in Italy: Modelling the interaction between intravenous drug users and heterosexual population", *Statistics in Medicine.* **11**(1992), 1657-1684.
3. P. Bacchetti, M.R. Segal and N.P.Jewell, "Backcalculation of HIV infection rates", *Statistical Science.* **8**(1993), 82-119.
4. R. Brookmeyer, "Reconstruction and future trends of the AIDS epidemic in the United States", *Science.* **253**(1991), 37-42.
5. R. Brookmeyer and A. Damiano, "Statistical methods for short term projections of AIDS incidence", *Statistics in Medicine.* **8**(1989), 23-34.
6. R. Brookmeyer and M.H. Gail, "A method for obtaining short-term projection and lower bounds on the size of the AIDS epidemic", *Journal of the American Statistical Associations.* **83**(1988), 301-308.
7. R. Brookmeyer and M.H. Gail, "AIDS Epidemiology : A Quantitative Approach", New York: Oxford University Press (1994).

8. F. Chiarotti, M. Palombi, S. Nicola, A. Ghirardini, and L. Prospero, "Effects of different parametric estimates of seroconversion time on analysis of progression to AIDS among Italian HIV positive haemophiliacs", *Statistics in Medicine.* **11**(1992), 591-601.
9. N.E. Day, S.M. Gore and D. De Angelis, "Acquired immune deficiency syndrome predictions for England and Wales (1992-1997): Sensitivity analysis, information, decision", *Journal of Royal Statistical Society A.* **158**(1995), 505-524.
10. M.J.R. Healy and H.E. Tillett, "Short-term extrapolation of the AIDS epidemic", *Journal of the Royal Statistical Society A.* **151**(1988), 50-61.
11. S. H. Heisterkamp, B. J. De Haan, J. C. Jager, J.A.M. Van Druten and J.C.M. Hendricks, "Short and medium term projections of the AIDS/HIV epidemic by dynamic model with an application to the risk group of homo/bisexual men in Amsterdam", *Statistics in Medicine.* **11**(1992), 1425-1441.
12. A.B. Mariotto, S. Mariotti, P. Pezzotti, G. Rezza, and A. Verdecchia, "Estimation of the acquired immunodeficiency syndrome incubation period in intravenous drug users: A comparison with male homosexuals", *American Journal of Epidemiology.* **135**(1992), 428-437.
13. H.C. Ong, S.H. Quah and H.C. Low, "An application of the backcalculation method to estimate past HIV infection rates in Malaysia", *The Medical Journal of Malaysia.* **53**(1998). 385-391.
14. J.M.G. Taylor, "Models for the HIV infection and AIDS epidemic in the United States", *Statistics in Medicine.* **8**(1989), 45-58.

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A study on shape analysis of structures under thermal loading with constraints in element strains

K.K.Choong*, Y.K.Chong and J.Y.Kim

*School of Civil Engineering, Universiti Sains Malaysia, Engineering Campus
Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia
cekkc@eng.usm.my

Abstract

Truss structures experience thermal loading due to heating. Changes in temperature will induce stress in the members and cause deformation of the structure. For long span truss structure, effect of such thermal loading might be especially critical in the sense that excessive deformation or failure due to over-stressing of members might occur. This paper is about shape analysis of truss structures subjected to thermal loading, with constraints in member strain. The governing equations for shape analysis are formulated by combining stiffness equation for truss structure and constraint equations. The existence condition of solution formulated with the use of generalized inverse matrix is adopted as the basis of the proposed iterative analysis. The results of one numerical example has been included to show the applicability of the adopted analysis strategy.

1 Introduction

Effect on stress as well as deformation due to thermal loading as a results of temperature changes might be especially critical in large-span lightweight truss structures. Fig.1 shows an example where members in large-span lightweight truss structures might experience thermal loading due to different changes in temperatures.

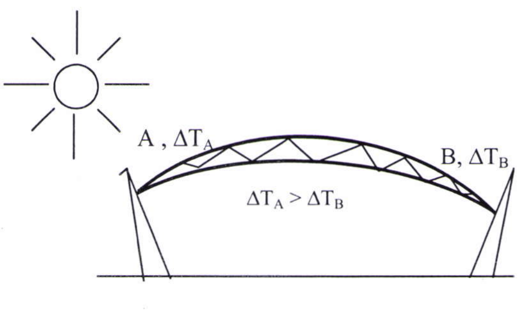


Fig. 1 : A large-span roof structure subjected to uneven exposure to sunlight

If $\boldsymbol{x}$ is a vector representing the shape of a structure and g_i is the i^{th} constraint function, then the process of shape analysis with constraints could be expressed as : Find $\boldsymbol{x}$ under the condition $g_i(\boldsymbol{x})\leq 0$ (i=1,2,...) with topology of structure kept unchanged. In this research study, member strain has been chosen as the constraint due to the reason that strain could be easily measured. Overstressing or excessive deformation of truss structure under the effect of thermal loading could be avoided by limiting the strain to suitable level. Results of literature review have shown that shape analysis with constraint by the use of generalized inverse has been carried out by various researchers [1-5]. However, shape analysis of truss structures under thermal loading with member strains as constraints has not yet been attempted. Due to this fact, the present study has been carried out with the objective of studying the applicability of a solution algorithm for shape analysis using generalized inverse for truss structures under thermal loading with members strains as constraints.

2 Basic formulation

Let us assume that the number of members and degrees of freedom of a truss structure are M and n respectively. Using a two-node truss element, force($\boldsymbol{F}$)-displacement($\boldsymbol{U}$) relation could be expressed as follows :

$$\boldsymbol{F} = \boldsymbol{KU} \tag{1}$$

where $\boldsymbol{F}=\Sigma \boldsymbol{f}$, $\boldsymbol{K}=\Sigma \boldsymbol{k}$, $\boldsymbol{f}$: equivalent member nodal force due to temperature change, $\boldsymbol{K}$: structure stiffness matrix, and Σ represents assembly process symbolically. $\boldsymbol{k}$ and $\boldsymbol{f}$ are given by the following two equations :

$$\boldsymbol{k}=\frac{E_e A_e}{l_e}\begin{bmatrix} l^2 & lm & -l^2 & -lm \\ lm & m^2 & -lm & -m^2 \\ -l^2 & -lm & l^2 & lm \\ -lm & -m^2 & lm & m^2 \end{bmatrix} \quad , \quad \boldsymbol{f}=E_e A_e \alpha \Delta T\begin{Bmatrix} -l \\ -m \\ l \\ m \end{Bmatrix} \tag{2}$$

where E, A, l_e :Young's modulus, cross-sectional area and length of member e respectively, l, m : directional cosine of member axis with respect to global x and y axes respectively, α : coefficient of thermal expansion and ΔT: change in temperature. Relation between member axial strain and nodal displacement is as follows:

$$\varepsilon=\frac{1}{l_e}\begin{bmatrix} -l & -m & l & m \end{bmatrix}\begin{Bmatrix} u_1 \\ v_1 \\ u_2 \\ v_2 \end{Bmatrix} \tag{3}$$

where u_j, v_j : global x and y nodal displacement (j=1,2), respectively. Expressing Eq.(3) in matrix notation as $\varepsilon_e = \boldsymbol{B}_e\boldsymbol{u}_e$ and assuming that strains in p($\leq M$) members are constrained to the prescribed values, then the p constraint equations could be expressed as follows:

$$\boldsymbol{\varepsilon} = \boldsymbol{BU} \tag{4}$$

where ε : vector of member strains with size p and $\boldsymbol{B} = \Sigma \boldsymbol{B}_e$. Combination of Eq.(1) and (4) will yield :

$$\boldsymbol{AU} = \boldsymbol{b}\text{, where } \boldsymbol{A}=\left[\frac{\boldsymbol{K}}{\boldsymbol{B}}\right] \text{ and } \boldsymbol{b}=\left[\frac{\boldsymbol{F}}{\boldsymbol{\varepsilon}}\right] \tag{5}$$

Since matrix $\boldsymbol{A}=\boldsymbol{A}(\boldsymbol{x})$ of Eq.(5) in this study is a rectangular matrix with size $(n+p) \times n$, it cannot be solved by using ordinary inverse matrix. Furthermore, since the shape of structure satisfying the prescribed member strain is unknown in the beginning of analysis, Eq.(5) has to be solved iteratively. Condition for the existence of solution for Eq.(5) as shown below is used as the basis of shape analysis in this study :

$$(\boldsymbol{I}_j - \boldsymbol{A}\boldsymbol{A}^+)\boldsymbol{b} = \boldsymbol{0} \qquad (6)$$

where $\boldsymbol{I}_j$: identity matrix of size $j \times j$ and $\boldsymbol{A}^+$: Moore-Penrose generalized inverse for $\boldsymbol{A}$. Here, generalized inverse[5] is adopted since $\boldsymbol{A}$ is not a square matrix. Since $\boldsymbol{A}=\boldsymbol{A}(\boldsymbol{x})$ as mentioned earlier, the task here now is to find $\boldsymbol{x}$ such that Eq.(6) is satisfied. Newton-Raphson iterative scheme has been adopted in this study. Denoting the left hand side of Eq.(6) as $\boldsymbol{g}(\boldsymbol{x})$ and linearizing it, the following equation will be obtained :

$$g(x_{i+1}) = g(x_i) + \nabla g(x_i)(x_{i+1} - x_i) \quad \text{, where } [\nabla g(x_i)]_{jk} = \frac{\partial g_k(x_i)}{\partial x_j} \qquad (7a,b)$$

$\nabla \boldsymbol{g}(\boldsymbol{x}_i)$ is the Jacobian matrix with size $(n+p) \times q$ where q: number of design variable and subscript in vector $\boldsymbol{x}$ represents iterative step. Assuming that the required shape is obtained at $(j+1)$-th iterative step, then the correction to vector $\boldsymbol{x}$ ($= \boldsymbol{x}_{j+1} - \boldsymbol{x}_j$ or $\Delta \boldsymbol{x}_j$) could be obtained from Eq.(7) and new shape updated as follows, respectively :

$$\Delta \boldsymbol{x}_i = -[\nabla g(\boldsymbol{x}_i)]^+ g(\boldsymbol{x}_i) \quad , \quad x_{j+1} = x_i + \Delta x_1 \qquad (8a,b)$$

Differentiation of $\boldsymbol{A}$ and $\boldsymbol{A}^+$ needed for the calculation of Jacobian matrix $\nabla \boldsymbol{g}(\boldsymbol{x}_n)$ could be evaluated using the following equation :

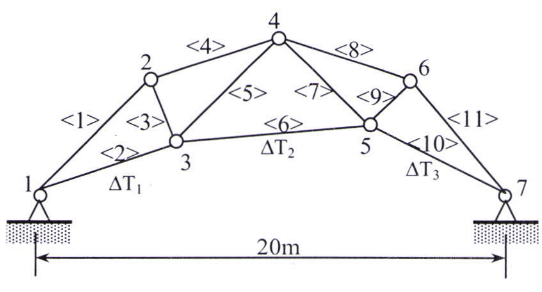
$$\frac{\partial \boldsymbol{g}(x)}{\partial x} = \frac{\partial \{A(x)A^+(x)\}}{\partial x} b(x) + [A(x)A^+(x) - \boldsymbol{I}_J] \frac{\partial \boldsymbol{b}(x)}{\partial x} \qquad (9)$$

where

$$\frac{\partial \{A(x)A^+(x)\}}{\partial x} = [\boldsymbol{I}_j - A(x)A^+(x)] \frac{\partial A(x)}{\partial x} A^+(x) + \frac{\partial A(x)}{\partial x} A^+(x)[I_j - A(x)A^+(x)] \qquad (10)$$

The procedures of analysis is started with the assumption of initial shape $\boldsymbol{x}_0$. This is then followed by the computation of $\boldsymbol{K}$, $\boldsymbol{B}$ in Eq.(5). After this step, constraints on member strains (ε_C in Eq.(5)) are prescribed and $\boldsymbol{F}$ in Eq.(5) is also computed. Matrix $\boldsymbol{A}$ and vector $\boldsymbol{b}$ in Eq.(5) are next formed. This is then followed by the evaluation of $\boldsymbol{g}(\boldsymbol{x}_i)$ and the subsequent solution of Eq.(8a) for $\Delta \boldsymbol{x}_i$. Using $\Delta \boldsymbol{x}_i$, the shape of the structure is then updated using Eq.(8b). This set of procedures is then repeated until the required shape is obtained. It is noted that $\boldsymbol{x}_0$ as mentioned earlier should be replaced with $\boldsymbol{x}_i$ for $i \geq 1$. More details could be found in Ref.[6].

3 Numerical example



Young's modulus :
$E = 200 \times 10^9 N/m^2$
Member area :
$A=0.05m^2$
Coefficient of thermal expansion :
$\alpha = 12 \times 10^{-6}/^\circ C$

$\Delta T_1=10^\circ C$
$\Delta T_2=20^\circ C$
$\Delta T_3=30^\circ C$

Coordinates of target shape :

Node	x	y
1	0	0
2	4	4
3	6	3
4	10	5
5	14	3
6	16	4
7	20	0

Fig.2 : Numerical example : a 11-member 2D truss

The example in Fig.2 has been analysed. For the analysis, a target shape $\boldsymbol{x}_{tar}$ is first identified. The truss structures with $\boldsymbol{x}_{tar}$ is then analyzed subjected to given patterns of temperature changes. The resulting member strain ε_c are adopted as the constraints. Shape analysis is then started with the initial shape $\boldsymbol{x}_0$ in which the joint coordinates are deviated uniformly from $\boldsymbol{x}_{tar}$ by three different levels of percentage: 1%, 3% and 5%. In this example, only coordinates of nodes 3 and 5 are allowed to change. Target joint coordinates are shown in Fig.2. Iterative calculation is then carried out until the convergent criteria is satisfied. Tables in Fig.3 and 4 show the analysis results. For table in Fig.4, only results correspond to percentage deviation 5% have been listed. In both figures, values in ( ) denote target values. From the results presented, it can be seen that convergence has been achieved after a maximum of 4 iteration (Fig.3). Comparison between joint coordinates and member strains of converged shape with the corresponding values of target shape has shown that the solution algorithm yield results with satisfactory accuracy (Fig.3 and 4).

% deviation		1 (ite=2)		3 (ite=3)		5 (ite=4)	
		initial shape	converged shape	initial shape	converged shape	initial shape	converged shape
Node	3	6.06	6.00(6.0)	6.18	6.00(6.0)	6.30	6.00(6.0)
		3.03	3.00(3.0)	3.09	3.00(3.0)	3.15	3.00(3.0)
	5	14.14	14.00(14.0)	14.42	14.00(14.0)	14.70	14.00(14.0)
		3.03	3.00(3.0)	3.09	3.00(3.0)	3.15	3.00(3.0)

Fig.3 : Results of analysis for numerical example : Joint x and y coordinates of converged shape

Member	1	2	3	4	5	6	7	8	9	10	11
Member strains in converged shape ($\times 10^{-6}$)	130.8 (130.7)	262.5 (262.4)	-129.2 (-129.2)	210.9 (210.9)	-94.2 (-94.2)	58.6 (58.7)	-44.1 (-44.1)	165.5 (165.5)	-101.4 (-101.4)	214.5 (214.5)	71.9 (71.9)

Fig.4 : Results of analysis for numerical example : member strains in converged shape (case of % deviation = 5%)

4 Conclusion

Shape analysis of truss structures under thermal loading with constraints in member strains has been studied. A solution algorithm involving the use of generalized inverse and Newton-Raphson iteration scheme has been adopted. Numerical results show that the accuracy of the adopted shape analysis strategy is satisfactory.

5 Acknowledgement

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References

[1] Guan F.L. Shape analysis with constraint in displacement mode. *Research Report on Spatial Structures*, Institute of Industrial Science and Technical Research Centre of Takenaka Corporation, Japan(in Japanese), 1990.

[2] Hangai, Y. and Kawaguchi, K. Analysis for shape-finding of unstable link structures in the unstable state. *Proc. of the International Colloquium on Space Structures for Sports Buildings,* Beijing, T. T. Lan and Y. Zhilian(eds). Science Press and Elsevier Applied Science, 1987; 104-111.

[3] Tanaka, H and Hangai, Y. Rigid body displacement and stabilization conditions of unstable truss structures, shells, membranes and space frame. *Proc. Of IASS* Symposium, Osaka, Volume 2, K.Heki(ed). Elsevier Science Publishers, 1988.

[4] Hangai Y. Shape analysis of structures. Theoretical and Applied Mechanics, Volume 39, *Proc. of 39th Japan National Congress for Applied Mechanics,* JNCTAM Science Council of Japan(ed). Univ. of Tokyo Press, 1990;. 11-28.

[5] Hangai Y and Kawaguchi K. Keitai Kaiseki (Shape Analysis). *Baifukan, 1991 (in Japanese).*

[6] Chong Y.K. Analysis Bentuk Struktur Terhadap Beban Suhu Dengan Kekangan Dalam Terikan Anggota Dengan Menggunakan Songsangan Teritlak. MSc Dissertation, School of Civil Engineering , Universiti Sains Malaysia, 2001.

Proceedings of the 5th International Conference on
Computation of Shell and Spatial Structures
June 1-4, 2005 Salzburg, Austria
E. Ramm, W.A. Wall, K.-U. Bletzinger, M. Bischoff (eds.)
www.iassiacm2005.de

Shell surface with folds - Mimicking idea from leaves of Johannesteijsmannia altifrons

Suhail A.Razzack, K.K.Choong*

*School of Civil Engineering, Universiti Sains Malaysia
Engineering Campus, 14300 Nibong Tebal, Pulau Pinang, Malaysia
cekkc@eng.usm.my

Abstract

Surfaces found in nature can serve as sources of idea which can be adopted for possible application in engineering structures. Of special interest are shell-like surfaces with folds which can be observed in leaves of many plants. In this research, the leaves of a majestic plant called Johannesteijsmannia altifrons which belong to the palm family will be investigated. The leaves of Johannesteijsmannia altifrons resembles a cantilevered shell structure with folds extending from the central spine. Such combination of shell surface and folds might have contributed to the ability of the leaves of Johannesteijsmannia altifrons to extend to a span of about 6m. Apart from such positive characteristic from the point of view of load carrying capacity, the existence of folds has also added element of aesthetic to the natural surface due to the interplay of shadows caused by the folds. In this paper, leaves of Johannesteijsmannia altifrons has been first measured using structured lighting method. Using the information obtained about the surface data as reference, procedures to generate shell surface with folds are then presented. The generated surface could be beneficially adopted as alternative "nature-like" new roof structural system.

1 Introduction

Using ideas from nature is justifiable based on the fact that existing natural systems could survive over thousands of years through adapting to the prevailing environmental conditions using nature's limited resources in an amazingly efficient manner. In case of engineering structures and materials the concern is cash cost whereas for living organisms, the cost is energy and the competition is not commercial but the more severe one of nature where the fittest survive and failures are fossils. Surfaces found in nature can serve as a source of idea which can be adopted for possible application in engineering structures. Among the natural sources of this kind are seashells and plant leaves where studies have been carried out (Jirapong and Krawczyk [3], Balz and Güring [1], De Focatiis and Guest [2], Kobayashi, Kresling and Vincent [4]).

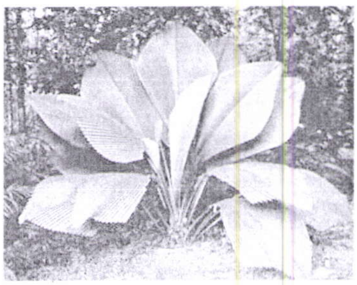

Fig.1 Johanesteijsmannia altifrons

In this study, the leaves of a majestic plant called Johannesteijsmannia altifrons (JA) which belongs to the palm family have been investigated(Fig.1). The leaves of JA resemble a cantilevered shell structure with folds extending from the central spine. Such combination of shell surface and folds might have contributed to the ability of the leaves of JA to extend to a span of about 6m. Apart from such positive structural merit, the existence of folds has also added element of aesthetic to the natural surface due to the interplay of shadows caused by the folds. In a pioneering work, Ng [5] has modeled the surface of JA and investigated the leaf behavior under load through finite element analysis.

This study has been attempted with the aim of presenting a process for the generation of doubly curved surfaces with folds that resemble the surface of JA – a natural object – which could possibly be adapted for engineering structures such as roofs

2 Surface data acquisition

Due to the very flexible/deformable nature of the leaf of JA, a non-contacting methods called structured lighting method is used to measure the surface. The experimental setup used in capturing the leaf images is shown in Fig.2. It is to be noted that the leaf pictures with shifted fringe on its surface is taken without cutting the leaf from its containing pot. This is an important aspect in order to compute a model that closely represents the leaf in its natural condition.

The principle used in getting the 3D surface data of the leaf is illustrated in the line diagrams of Fig.3. In Fig.3, S is the measured shift in fringe which is used to obtain Z through the following equation : $Z=S/\tan\theta$. Fig.4 shows the captured image which is used in calculating the 3D coordinates with the help of the shifted fringes over the surface of the leaf. The final result in the form of mesh is shown in Fig.5. The results obtained are quite representative to reflect the actual shape of the leaf.

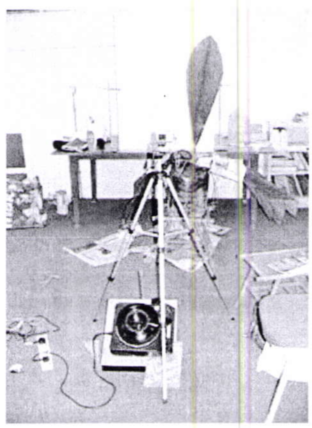

Fig.2 : Set-up for measurement of leaf of JA

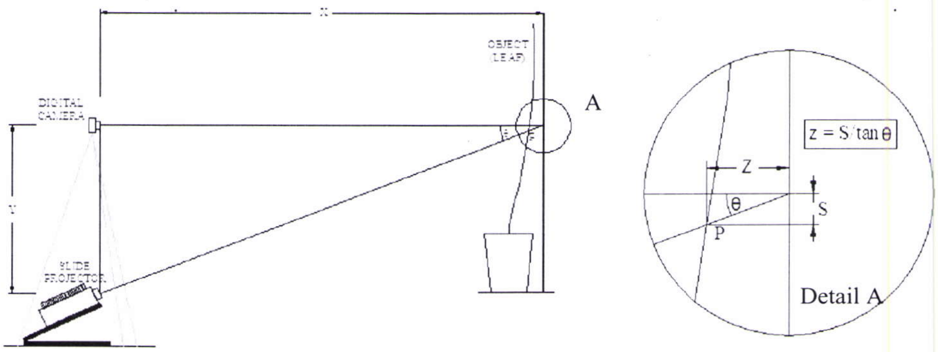

Fig.3 : Schematic diagram of the set-up for measurement of leaf of JA and the detail at A

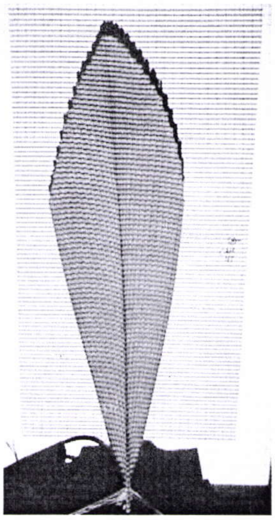

Fig.4 : Image of leaf of JA with fringe projections

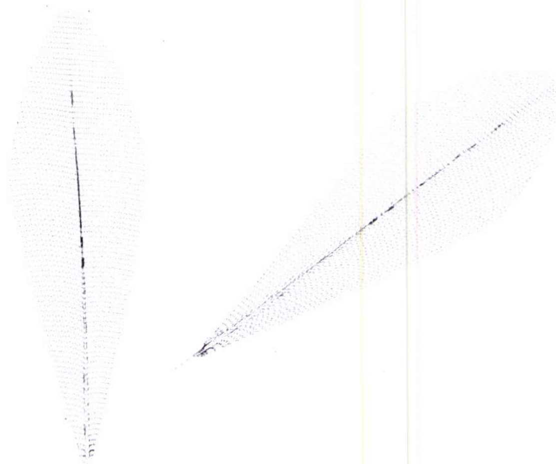

Fig.5 : Surface data obtained for leaf of JA

3 Generation of doubly curved folded surfaces based on idea from leaf of JA

This paper presents one possible approach in generating doubly curved folded surfaces which mimic the idea of leaf of JA. Figs.6 to 13 show the process of generation by utilizing the 3D modeling options available in CAD software. It can be observed that the end result resembles a doubly curved surface with folds. Fig.14 shows a possible shape of roof structure which can be generated through assemblage of six numbers of unit folded surface.

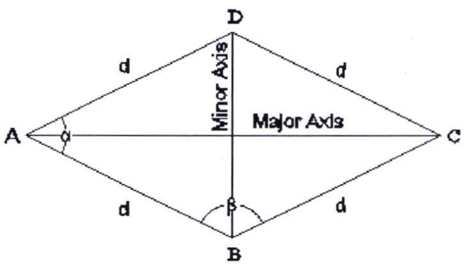

Fig.6 : Step 1 - The starting figure

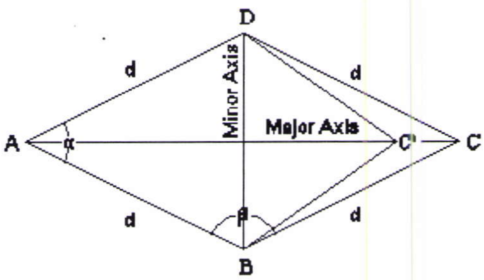

Fig.7 : Step 2 - C is tilted to C'

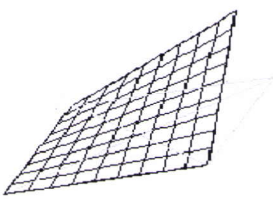

Fig.8 : Step 3 - ABC'D is meshed

Fig.9 : Step 4 - Lines AC' and BD are drawn

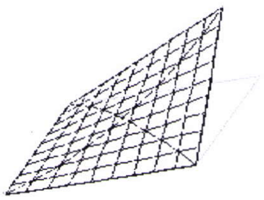

Fig.10 : Step 5 - Identical surface is created by shifting

Fig.11 : Another view of result in Step 5

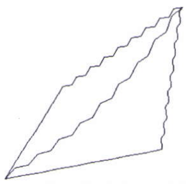

Fig.12 : Step 6 - Zigzag boundary is formed between the two surfaces

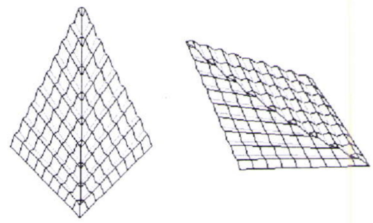

Fig.13 : Step 7 - Folds are generated and doubly curved folded surface is formed

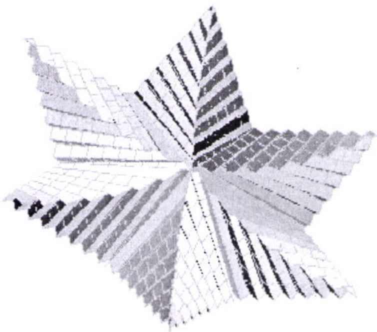

Fig.14 : One possible shape of roof structure with six number of unit folded surfaces

4 Conclusion

Structured lighting method has been applied to generate a 3D folded surface of the leaf of JA. The result obtained is found to be quite representative. Procedures to generate a nature-inspired doubly curved folded surface has also been presented. The value of this study is the relatively simple process of developing doubly curved folded surfaces that can be used as possible choices for roof structures.

5 Acknowledgement

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References

[1] Balz, M. and Güring, J. J. Botanic Shell Structures. *IASS 2001*, Nagoya, Japan, 2001. http://www.ifp.uni-stuttgart.de/publications/2001/pub2001.html.

[2] De Focatiis, D. S. A. & Guest, S. D. Deployable Membranes Designed from Folding Tree Leaves. *Phil. Trans. R. Soc. Lond. A*. 2002

[3] Jirapong, K. & Krawczyk, R. J. Seashell Architectures. *ISAMA/Bridges Conference*, July,2003. http://www.iit.edu/~krawczyk/

[4] Kobayashi, H., Kresling, B. & Vincent, J. F. V. The Geometry of Unfolding Tree Leaves. *Proc. R. Soc. Lond. B* 1998; 265: 147-154.

[5] Ng, K. W. A Study of Load Carrying Characteristics of A Surface Modeled After A Folded Leaf. MSc Dissertation. School of Civil Engineering, Universiti Sains Malaysia. 2003

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ETHICAL BUSINESS DECISION: THE QUESTION OF MORAL DEVELOPMENT

27566

Nabsiah Abdul Wahid
Universiti Sains Malaysia

Haslida Abu Hasan
Universiti Teknologi PETRONAS

Abstract

Moral development is always seen as part of a person's total intellectual and emotional development. Moral development contributes to moral reasoning and therefore resulted in moral judgment and determined choice of action, which can be evaluated as ethical or unethical. Moral development and character formation comes hand in hand. Character, good or bad, is observable in one's conduct. Character is different from values in that values are orientations or dispositions whereas character involves action or activation of knowledge and values. How do we value ethics depends on our moral development that formed our character and therefore affect our judgments and actions. In this new era, we have seen a lot of business failures due to unethical decisions made by management and executives. Therefore, there is a need to look back at the root cause determining the decision making process of individuals in business. This paper will discuss the issues pertaining to moral development and its contribution to ethical business decisions. An exploratory study on factors influencing ethical behavior and business ethics curriculum has been conducted and the result is presented and discussed.

Keywords: moral reasoning, moral development, business ethics.

INTRODUCTION

The ethics of business is currently a high profile issue and receiving increased attention across various business disciplines due to at least, in part, to the scandals and negative publicity that have plagued business and government in recent decades. This contributes to increased social pressure on companies to adopt a more socially responsible approach to doing business (Malachowski 1992; Evans 1991). Example of prominent incidents and issues that have provoked controversy over organizational ethical conduct include: top executives being caught on tape displaying discriminatory attitudes toward minorities, savings and loan failures, insider trading fraud, toxic waste disposal, product safety issues and governmental officials accepting gifts that raise conflict of interest questions.

Businesses, besides providing return to owners, is charged with other tasks like acting lawfully, producing safe products and services at costs commensurate with quality, paying taxes, creating opportunities for wealth creation through jobs and investments, commercializing new technologies, and minimizing negative social and environmental impacts. Unless management attends to all its responsibilities, achieving fair returns to shareholder will not be possible[1]. Organizations may possibly face public scrutiny over their ethically questionable actions by investigative reporters or/and public interest group. Companies may also have to bear the high cost of unethical behaviors such as fines, embarrassment, the loss of public confidence and reputation, low employee morale, a disruption in normal business routine and difficulty in recruiting[2].

Ethics and Business

It is no doubt that people who are directly involved in business and management positions like the managers, marketers, accountants and financiers constantly face ethical dilemmas in today's modern business world. As ethics is generally refers to human involvement in moral issues of right and wrong, people like accountants must avoid actions which actively (or passively) prejudice responsible judgment or successful performances of an activity in which they have direct influence [3 Sept 2001, http://www.greenconsumerguide.com/article177.html]. Various models have been proposed in the business ethics literature to identify the important influences on ethical decision-making (Bommer et al., 1991; Jones, 1991; Hunt & Vitell, 1986; Trevin & Youngblood, 1990; Ferrell et al., 1989). These models recognize the importance of moral reasoning to ethical decision-making. Moral reasoning involves how ethical decisions are arrived at, i.e. on what basis these decisions are supported or justified. In the pursuit of preventing unethical behaviors, university educators are placing increased emphasis on ethics in the classroom. The American Assembly of Collegiate Schools of Business (AACSB), a prominent accreditation body for business schools, identifies ethics as an important component of the undergraduate business curricula. In addition, various professional organizations and companies have issued codes of conduct to provide guidance for their members to resolve ethical issues.

However, in the light of growing concern over the apparently low moral standards of some accountants, an increasing number of academics are suggesting that the education system should bear some of the blame (Gray et al 1994; Booth & Blundell 1988; Lehman 1988; and by implication Power 1991). They contend that we need to re-examine the type of educational system that produces accounting professionals who, consciously or otherwise, appear to act unethically (see Loeb & Rockness 1992; Gray et al 1994; Mahoney 1990). Merritt (1991; see also Zeff 1989) for example contents that education is the crucial issue in business ethics, he concludes, 'business schools have not done an adequate job of preparing students to respond ethically to the complex issues that arise in the work environment.'

Can we achieve an ethical businessperson through educating students with business ethics? Many studies have been done on different groups of students and proved that ethical decision making differs across groups being a business majors having more tendency to act unethically as compared to science and art majors (Hendrickson and Latta, 1995)[3]. Rick Tetzeli (1991) for example found that out of 15000 university students who were surveyed, more than 76% of business students admitted that they have cheated in a way or two compared to those coming from six other areas. Similarly Davis and Welton (1991) argue

[1] Report of the Ethics Education Task Force on Ethics Education in Business School, AACSB International, 2004

[2] John C Windsor, "A Comparative Study of Moral Reasoning, College Student Journal, June 1999 (http://www.findarticles.com/)

[3] Other research done across groups were Stevens et al. (1993), Glenn and Van Loo (1993), Arlow and Ulrich (1985), Paradice and Dejoice(1991), Kievet(1991).

that, 'Part of the long-term solution to improving professional ethics is to address the area as it relates to educating future business professionals, i.e. college students.' While the evidence is still unclear, a growing body of research suggests that rather than contributing towards students' moral development, compared with other professions, accounting education may actually stultify students' progression to higher levels of moral reasoning and ethical awareness (See Gray et al 1994).

While the evidence from both the business press and the business ethics literature (see for example McCabe et al 1991; Ponemon 1990; 1992; Gavin & Klinefelter, 1989 and Armstrong 1987) appears, to some extent, to substantiate Merritt's conclusion, Ken McPhail (1997) wrote arguments on the potential threats posed by ethical accountants. In his paper he presented an alternative, although not entirely incongruous, Foucauldian analysis of the relationship between accounting education and ethics. The paper contends that there may be a more fundamental though less obvious ethical dilemma to be addressed. It was suggested above that it is professional accountants who seem to be amongst the main contributors to the decline in ethical standards within business (McCabe et al 1991; Modic 1987, in Davis & Welton 1991; Hauptman and Hill 1991).

However, while the unethical behavior of some accountants presents a major challenge to the profession and educationalists alike, his paper argues that the greater problem and indeed threat to society may actually come from the majority of accounting professionals who behave ethically! [14 July 2004, http://les.man.ac.uk/ipa97/papers/mcphai46.txt]. In the paper he apply Michel Foucault's work on ethics to accounting education in order to consider how power may be seen to operate through the discourse of accounting education in a hegemonic and threatening way. The paper draws on Foucault's work on ethics to argue that, it may not just be that accounting education stultifies students' moral development, but that it actually provides them with a moral identity which not only covertly serves capitalism but also the kind of instrumental rationality upon which it is based (see McPhail & Gray, 1996).

The paper suggests that accounting education may implicitly provide students with an ideal model of the ethical and just individual, which they subsequently use to discipline themselves in order to behave properly and remain as close to that ideal as possible. As such, it will be argued that, while Merritt's (1991) observation is undoubtedly true, there may be a sense in which business education does prepare students for responding to ethical issues through effectively constructing their moral identities. It will be contended that accounting education in particular can be seen to be involved in complex hegemonic processes where power and control are affected in society not by one group on another in an overt way, but rather by individuals upon themselves. Accounting is based on the set of generally acceptable standards and procedures, which allows for various treatment and therefore contributed to 'creative accounting' activities whereby accountants can use their knowledge of accounting rules to manipulate the figures reported in the account of the business. In view of creative accounting, ethical issues are quiet vital due to the practice which normally serves companies' or shareholders' interest, what about society at large?

Several perspectives to look at in considering creative accounting, which is popular and ethical consideration:

Griffiths (1996) writing from the perspectives of a business journalist observes: "Every company in the country is fiddling its profits. Every set of published accounts is based on books, which have been gently cooked or completely roasted. The figures, which are fed twice a year to the investing public, have all been changed in order to protect the guilty. It is the biggest con trick since the Trojan horse....In fact this deception is all in perfectly good taste. It is totally legitimate. It is creative accounting"(p1).

Jameson (1988) wrote on the perspective of the accountant: "The accounting process consists of dealing with many matters of judgment and of resolving conflicts between compelling approaches to the presentation of the results of financial events and transactions (p7),....this flexibility provides opportunities for manipulation, deceit and misrepresentation. These activities- practiced by the less scrupulous elements of the accounting profession-have come to be known as 'creative accounting' (p8). From the academic's view, Naser (1993) defines: "creative accounting is the transformation of financial accounting figures from what they actually are to what preparers desire by taking advantage of the existing rules and/or ignoring some or all of them" (p.2)

Moral Development and Reasoning

A person's morality is influenced by a variety of internal and environmental factors. In one conception, moral action is determined by four components: (1) moral sensitivity (comprehending moral content when present in a situation), (2) moral judgment (determining what is the moral thing to do), (3) moral motivation (choosing to do what moral rather than other values dictate), and (4) moral character (having qualities such as strength of ego, perseverance, and courage to act)[4]. All four of these components, and perhaps others, work together to influence a person's behavior. Development in one component does not guarantee development in another; all four are necessary for moral action. Of the four components, moral reasoning or judgment is the most fully researched. It is a cognitive variable, which we know colleges and universities can have a powerful impact.

What is moral reasoning? Human nature is naturally good. At least it leans decidedly toward an awareness of the good, and a preference for it, over evil and injustice. Despite appearances, human nature is inherently self-realizing and self-perfecting, if in moral understanding and aspiration more than practice. Moral development grows in human beings spontaneously alongside physical limbs, basic mental and social capacities. Both individually and in social interaction the human species evolves mature moral conscience and character despite the many psychological and social impediments that slow or re-dial the process for a time. During 1970s, psychologists revalued cognitive development theory. Researchers such as Lawrence Kohlberg, Benjamin Bloom and Howard Gardner derived their theories from Piaget's stage development theory, which says that children progress from intuitive, to concrete and then to abstract thinking. Lawrence Kohlberg developed his model of moral development from Piaget, introducing a new methodology into his research, using moral dilemma as a way of assessing people's reasoning styles[5]. Kohlberg's introduces a stage model, human beings will developed through all this three stages of moral reasoning; Pre-Conventional morality, Level 1, where a person's ethical decisions are motivated by seeking reward and avoiding punishment rather than moral principle (don't hit it because you'll get into trouble), Conventional morality, Level 2, people are concerns with reciprocal fairness (don't hit or you might get hit back), living up to the expectation of relevant others and upholding the law, Post-conventional morality, Level 3, is a principled decision-making,

[4] Data are drawn from this two sources of research: Rest & Narvaez, 1994; Rest, Narvaez, Bebeau, & Thoma, 1999)

[5] Based on Dodd, J.M. and Menz, O., (1996), "Stewardship: a concept of moral education"

where one's decisions is based socially recognized codes and rules, (I'm a good person because I keep the rules).
Each of the three levels in Kohlberg's theory has two stages[6]:

Stage 1: Personal Survival-Acting upon survival instincts and never expects anyone to help. These people just take what they need without consideration of the impact on others. (Some individuals lapse into this under stress).

Stage 2: "You scratch my back, I'll scratch yours"-Recognize that others can help you, and that you must return the favor! (This probably be the level of politics and politicians-still no altruism)

Stage 3: Good and Bad-Behavior is dictated by whether it is seen as good or bad depending upon whether it conforms or goes against some learned doctrine of acceptable behavior.(Typical of many religious fundamentalists and peer pressure- altruism is only in seeking the approval of others).

Stage 4: Law and Order-Recognition that behavior needs to conform to written laws. (The law is the final arbiter and is seen as something that should be obeyed without question.-altruism is seen as a responsibility)

Stage 5: The Social Contract- Recognition that laws exists for the common good, but that these laws must not be viewed as applying in every case. There is a genuine interest in the welfare of others and the concept of justice-altruistic. (This stage is typical of those who protest the inequities of the system, go to jail on social principles, etc)

Stage 6: Recognition of Universal Principles-The individual fully realizes that there is a 'higher law' to which we are all subject. The individual highly evolved conscience as the sole of basis for behavior. Most behaviors are for the benefit of others. These people are willing to risk their lives for others.(The ultimate example being Christ)

Kohlberg postulated that each individual must go through each stage and cannot skip stages. The way that people progress is through social interaction and exposure to individuals that exhibit these "higher" traits. Through encounter with "moral dilemmas" people get to test their beliefs against those of others and thereby learn which belief system yields a more acceptable result. According to Kohlberg, children usually develop through stages 1 and 2 and settle into stages 3 and 4. A minority of adults passes into higher stages of 5 and 6. Most people, including college undergraduates, primarily use the moral reasoning of Conventional stages 3 and 4. As those stages are developed gradually, many people never develop the capacity for substantial Post-conventional reasoning. Developing upward through various stages, one's reasoning is increasingly concerned with others' needs and less exclusively with one's own.

Moral reasoning was commonly assessed using the popularly used test called the Defining Issues Test (DIT). The DIT (Rest, 1979) assesses how people justify or support their ethical decisions in terms of Kohlberg's (1969) levels of moral reasoning. College experiences can have a significant impact on students' moral reasoning. Some of the strongest college effects found in the literature are on moral reasoning (McNeel, 1994).The impact is particularly strong in liberal arts colleges and in disciplines that explore people and values. Students in more vocationally oriented disciplines such as business and education have shown considerably lower DIT score growth over their college experience. McNeel, 1994 has

[6] Quoting the explanation at Kohlberg's Theory of Moral Development Skip's Corner-Spirituality-Hippyland

remarked, "There may be moral development problem nationally in the areas of business and education,".

Numerous studies in moral education suggest practical tactics teachers can use that will help their students move towards more complex, principled ethical reasoning. Listed here are some methods consistent with the findings of research by Gardiner on fostering students' moral judgment.

- ✓ Have students discuss controversial moral dilemmas. Identify disciplinary issues with moral content-that relate to moral values. Develop cases, problems, or scenarios that involve these values for students to discuss.
- ✓ Have students play the roles of and explain the reasoning used by others to resolve moral dilemmas.
- ✓ Allow students to discover how various cultural groups reason about moral issues.
- ✓ All courses, even in disciplines such as mathematics or statistics that on their surface may appear to lack obviously moral content, offer rich opportunities for helping students develop their skill in moral reasoning. Every course can become a learning community where values of mutual respect, sensitivity to others' needs, and cooperation are emphasized and discussed.
- ✓ Ensure all students have ample out-of-class contact with faculty members.
- ✓ An addition to high involvement tactics, directly teach Kohlberg's model of six stages of reasoning as one would teach other, disciplinary concepts.
- ✓ Use the DIT to help both teacher and students understand their moral reasoning and track and improve program effectiveness.

A study done on IS professionals versus IS students found that the professionals use the highest level of Kohlberg's model (the post-conventional level) significantly more frequently that the students in making ethical decisions (J.C. Windsor, 1999). The finding was consistent with prior DIT research, which has found that age and number of years of formal education are positively related to principled moral reasoning scores (Trevino, 1992). Result of those studies suggested the importance of ethical training and education. Effective ethical problem solving is often more complex than many people realize. It involves the ability to identify ethical issues when confronted with them, to be cognizant of affected parties and the potential consequences of alternative actions, and to consider one's own duties and obligation to arrive at well-reasoned ethically defensible positions. There are several different models for the classification and description of moral decision-making. Rest's Four-component model represents this process as follows:

Step 1	It must be recognized that there is a moral issue involved. The decision maker must be able to appreciate that a selection of a particular course of action will affect the welfare of other interested parties.
Step 2	The decision maker must be able to select the action, which is morally correct or just.
Step 3	The decision maker must attach priority to moral values, rather than -say-acting out of self-interest.
Step 4	The decision maker must have sufficient moral strength to implement the decision taken in Steps 2 and 3 above.[7]

[7] Based on Rest, J.R., Moral Development: Advances in Research Theory, Praeger Publishers, New York, 1986a, as quoted by John Dunn, John McKernan, Patrick O'Donnell in " The Ethical Development and Socialisation of Accountants"

A survey conducted by Spears' (1973) of an education honorary society in America on goals of education showed the following ranking of goals of public schools:

1. develop skills in reading, writing, speaking and listening;
2. develop pride in work and feeling of self worth; and
3. develop good character and self-respect

In terms of defining good character, educators stated that this should include developing moral responsibility and sound moral and ethical behavior, capacity for discipline, a moral and ethical sense of the values, goals, and processes of a free society and standards of personal character and ideas. However, since 1930's American education has increasingly turned away from character education as a primary focus (Power, Higgens & Kohlberg, 1989) This is in spite of the fact that both educators and the public believe character education to be an important aspect of schooling.

Good character is defined in terms of one's actions[8]. Character development traditionally has focused on those traits or values appropriate for the industrial age such as obedience to authority, work ethics, working in groups under supervision, etc. However SCANS report (1991) and Huitt's (1997) critique has suggested that modern education must promote character based on values appropriate for the information age: truthfulness, honesty, integrity, individual responsibility, humility, wisdom, justice, steadfastness, dependability, etc.

Campbell and Bond (1982) propose the following as being the major factors that influences character development-moral development and behavior of youth (in contemporary America):

1. heredity
2. early childhood experience
3. modeling by important adults and older youth
4. peer influence
5. the general physical and social environment
6. the communication media
7. what is taught in the schools and other institutions
8. specific situations and roles that elicit corresponding behavior.

Exploratory Study on Perception

It is important to realize that while schools do and should play a role in development of character, families, communities, and society in general also have an important influence (Huitt, 1999). Various studies and literatures have point to an important issue of what actually determines ethical behavior. Therefore, there is a question as to whether business ethics' behavior can be developed through one's personal background or education. This question motivates the authors to conduct an exploratory study on a few Malaysian with the objectives of preliminary understanding on what actually influence ethical business decisions.

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[8] Educational Psychology Interactive: Moral and Character Development, page 3-13, (Walberg & Wynne, 1989-character is observable in one's conduct).

METHODOLOGY

The authors used convenient sampling technique to get a group of respondents in Malaysia. A questionnaire with more than fifty business ethics statements related to their beliefs and perceptions were distributed to the respondents to answer. Using a 5-point Likert scale, they were asked to indicate their level of agreement-disagreement to the statements made. However for the purpose of this paper, only selected statements will be used for analysis. It is important to note that only descriptive analysis will be discussed.

SURVEY RESULT AND DISCUSSION

Respondents' Profile

Of the total 200 respondents participated in the survey, the group is dominated by female (67.5%), those within the 20-29 years old age group (58.5%), the Malay ethnic (54.0%), and those who have good education background with tertiary education or similar (59.0%). The full profile is given in TABLE 1. To answer the questions of whether a person's personal background may have a role in influencing his/her ethical behavior, and, whether we can achieve an ethical business persons through educating a person with business ethics (BE), twelve specific statements from the questionnaire have been chosen for discussion here. Full results of these twelve statements can be found in TABLE 2. The twelve statements chosen were focused on two categories: factors influencing ethical behavior (statement 5 to 12) and BE curriculum (statement 1 to 4). As can be seen from the results, the findings indicate agreement with all the twelve statements that have been asked to the respondents.

TABLE 1: Respondents' Profile

Characteristic	Unit	Percentage (%)
1. Gender		
- male	65	32.5%
- female	135	67.5%
2. Age		
- below 20 years.	22	11.0%
- 20-29 years	117	58.5%
- 30-39 years	37	18.5%
- 40-49 years	19	9.5%
- 50 years old and above.	5	2.5%
3. Ethnic Group		
- Malay	106	54.0%
- Chinese	85	42.5%
- Indian	7	3.5%
- other ethnic.	2	1.0%
4. Highest level of education		
- University Degree/Professional.	118	59.0%
- STPM/HSC/Matriculation	59	29.5%
- College Diploma	14	7.0%
- SPM/SPVM/MCE.	6	3.0%
- PMR/SPP/LCE	1	0.5%
- primary school or below	0	0%
5. Occupation		
- Student	129	64.5%
- Government Employee	43	21.5%
- Private Sector Employee	24	12.0%
- housewife/househusband	3	1.5%
- Self Employed	1	0.5%
- Other	0	0%

Factors influencing ethical behavior

The question of what factors will influence one's ethical behavior was answered through eight statements. The majority of respondents were found to agree that ethical behavior depends on multiple factors that were believed to be more influential than what is taught in the curriculum. Those are: home/family values (statement 5), personal business experience (statement 6), business peers/friends (statement 7), perceived business profits (statement 8), religious beliefs (statement 9), authority/superior as a model's behavior (statement 10), personal belief that one must strive all out in order to succeed (statement 11), and personal belief of own social responsibility (statement 12).

BE curriculum

In terms of BE curriculum, we found that respondents believed BE should not only be incorporated into any business curriculum one is involved in (statement 1). It is quite interesting to see the majority agree that BE should be incorporated into every business course taught (statement 2), and that it should also be treated as a course on its own (statement 3). These positive results may be due to their belief that BE learned can actually influence how one should act when ethical consideration is sought (statement 4).

TABLE 2: Respondents' Dis/Agreement on Business Ethics Statements

Statement	Unit	Percentage (%)
1. Business ethics should be incorporated into the business curriculum one is involved in (e.g. when studying, or in training) - agree - disagree	 179 21	 89.5% 10.5%
2: Business ethics should be incorporated into every business course taught. - agree - disagree	 101 17	 50.5% 8.5%
3: Business ethics should be treated as a course on its own in the curriculum. - agree - disagree	 171 29	 85.5% 14.5%
4: Business ethics learned from the business curriculum will influence one to use the knowledge when the situation requires. - agree - disagree	 178 22	 89.0% 11.0%
5: How one is brought up by his/her family will influence his/her behavior more than what he/she is taught in school/universities' curriculum. - agree - disagree	 181 19	 90.5 9.5
6: One's experience of marketing business will influence his/her behavior more than what he/she is taught in school/universities' curriculum. - agree - disagree	 179 21	 89.5% 21.0%
7. The ethics taught in the curriculum is not as influential as what business peers can do to a person's behavior in the marketplace. - agree - disagree	 182 18	 91.0% 9.0%
8. The ethic taught in the curriculum is not as influential as what perceived profits that can be made in business can do to a person's behavior in the marketplace - agree - disagree	 185 15	 92.5% 7.5%
9. The ethics taught in the curriculum is not as influential as the religion beliefs one practices of what he/she should behave in the marketplace. - agree - disagree	 175 25	 87.5% 12.5%
10. The ethics taught in the curriculum is not as influential as how one perceived his/her boss/supervisors' behavior should be followed in the marketplace. - agree - disagree	 171 29	 85.5% 14.5%
11. The ethics taught in the curriculum is not as influential as the belief one has that he/she should try everything to succeed no matter what in the marketplace. - agree - disagree	 180 20	 90.0% 10.0%
12. The ethics taught in the curriculum is not as influential as the belief one has that he/she should be responsible for everything that happens to the community (i.e. consumers, society) in the marketplace. - agree - disagree	 171 29	 85.5% 14.5%

DISCUSSION

It is quite disappointing to see that although what is learned through BE is useful when the situation arises, it is other factors that actually dictates how one will behave – whether ethically or unethically. It is implied from the findings of this survey that environment plays significant role in molding one's ethical behavior (moral development). An individual is exposed to various environments – i.e. his/her home (different values and life styles) and social groups (friends, superiors). Thus, one may easily learn different attitude and behavior in which s/he can adapt or adopt to suit his/her own moral development. The process of learning can possibly be within a short or long span of time period. For example, a family value has been instilled in oneself since one is small, and thus will usually stays with him/her throughout his/her life. These values may actually influence a person's self-concept (that include intrinsic and extrinsic motivation) and the will to succeed in life. Success can be achieved through many ways, unfortunately unethical behavior is one aspect that some people resort to adopt, especially when lucrative business profits is perceived as the outcome.

So, coming back to the question as to whether BE education can influence one's ethical behavior, we can say that the answer is yes. If yes, then how do we do it? It is through identifying and understanding our fellow students' background before we start developing the BE curriculum. Once we know who they are, what their beliefs and aspirations are, etc. we can develop specific curriculum that can address specific problems and to guide them to develop good character and self-respect. According to Campbell and Bond's (1982) propositions, at least there are eight aspects that influence character development-moral development. One of them is "what is taught in the schools and institutions". Thus, we believe that in this study, it does.

CONCLUSION

Though ethics courses taught at school are not as influential as compared to childhood development and organizational culture, it does help in nurturing the development of moral reasoning and judgment. Possibly it will at least provide some knowledge, background or basis to a person's action. So, management educators need to think more deeply and creatively on how to advance the awareness, reasoning skills, and core principles of ethical behavior that will help guide business leaders as they deal with a changing legal and compliance environment. As suggested by Pascarella (1997), students must be grounded in the duties and rewards of stewardship, including the concerns of multiple stakeholders and the responsible use of power.

It is essential for business and management students to understand the symbiotic relationship between business and society, especially in terms of the moral dimensions of power placed in the hands of owners and managers. The actions of business leaders will not only affect themselves, but customers, employees, investors, suppliers, governments, citizens, and communities.

Business also has the responsibility to foster improved conditions for wealth creation. It must enhance its own future success and its ability to create more wealth by contributing to the communities where it hopes to prosper. The responsibilities of business go far beyond a financial accounting concern for the bottom line of short-term profit and loss. Emerging conceptual frameworks, such as social reporting, social impact management, and triple bottom line, can help business to assess these broader responsibilities.

Business schools should help students to see the criticality of ethical leadership to effective and successful management. Significantly, findings from cognitive moral development research verify that most working adults are at the conventional level of cognitive moral development. That is, they look outside themselves, primarily to peers and leaders, for guidance in ethical dilemma situations. The messages leaders send and the contexts they create are potentially the greatest motivating force behind ethical conduct in business organizations. To be considered as ethical leaders, executives must be both "moral person" and "moral managers". As noted in the literature, executives become moral persons by expanding their awareness to include multiple stakeholder interests and by developing and applying their own ethical decision-making skills to organizational decisions in ways that are transparent to their follower. Executives become moral managers by recognizing and accepting their responsibility for acting as ethical role models. Most students will not be executives early in their careers; but they need to understand that, even as supervisors, they will play a key ethical role in the organization by influencing the daily conduct of their direct reports.

References

Armstrong, M.B.,(1987), "Moral Development and Accounting Education", Journal of Accounting Education, pp. 27-44

Armstrong, M.B.,(1993), "Ethics and Professionalism in Accounting Education", Journal of Accounting Education, pp. 1-14

Dodd, J.M. and Menz, O.,(1996), "Stewardship: a concept in moral education", http://www.nexus.edu.au/teachstud/gat/dod_men1.htm, (18/01/2005)

Dellaportas, S., Leung, P., Cooper, B.J.,(2004), "Measuring Moral Judgment Using Accounting and Social Dilemmas", Asia Pacific Interdisciplinary Research in Accounting Conference, Singapore.

Derry, R.,(1989), "An Empirical Study of Moral Reasoning Among Managers", Journal of Business Ethics, Vol. 8, pp. 855-862

Dunn, J., McKernan, J., O'Donnell, E., (2003), "Moral Reasoning and the Accountants: Rules and Principles", ACCA Occasional Research paper No. 36.

Gardiner, L. F., "Fostering Students' Moral Development", (11/01/2005), http://ase.tufts.edu/cae/tufts-secure/v11/v11n5.htm

McNeel, S.P.,(1994), "University Teaching and Student Moral Development", Moral Development in the Professions: Psychology and Applied Ethics, Editors: Rest, J.R., and Narvaez, D., 27-49, New Jersey: Lawrence Erlbaum Associates.

McPhail, K.,(1999), "The threat of ethical accountants: an application of Foucalt's concept of ethics to accounting education and some thoughts on ethically educating for the other", Critical Perspectives on Accounting, Vol. 10, pp. 833-866.

Piaget, J.,(1965), "The Moral Judgment of the Child", Gabain, M. Trans, New York: The Free Press(originally published, 1932)

Ponemon, L.A., (1990), "Ethical Judgments in Accounting: A Cognitive-Developmental Perspective", Critical Perspectives on Accounting, pp.191-215.

Ponemon, L.A.,(1993), "Can Ethics Be Taught In Accounting?", Journal of Accounting Education", pp.1-29.

Pascarella, E.,(1997), " College's Influence on Principled Moral Reasoning", Educational Record, pp 47-55

Pascarella, E., Terenzini, P.,(1991), " How College Affects Students: Findings and insights from 20 years of research", San Francisco: Jossey-Bass

Tetzeli, R.,(1991), "Business Students Cheat the Most", Fortune, 1 July, pp. 14-15.

Rest, J.R.,(1979), "Development in Judging Moral Issue", Minneapolis:University of Minnesota Press.

St. Pierre, K.E., Nelson, E.S., and Gabin, A.L.,(1990), "A Study of the Ethical Development of Accounting Majors in Relation to Other Business and Non-business Disciplines", The Accounting Educators' Journal, pp. 23-25.

Ursery, D., "Introduction To Moral Reasoning", http://www.stedwards.edu/ursery/IntroMS.htm, (05/01/2005)

Windsor, J. C., (1999), "A Comparative Study of Moral Reasoning", College Student Journal, (http://www.findarticles.com)

AACSB International, (2004), "Ethics Education in Business School", Report of the Ethics Education Task Force.

http://www.education.uiowa.edu/epls/faculty/pascarel, (18/01/2005)

http://www.greenconsumerguide.com/article177.html, (03/09/2001)

http://les.man.ac.uk/ipa97/papers/mcphai46.txt, (14/07/2004)