Vol. 56 No. 1 February 1992

NZIC

Chemistry

IN NEW ZEALAND

SPECTROSCOPY

CHROMATOGRAPHY

PRECISION with SIMPLICITY

LETTER FROM THE PRESIDENT

Dear Member
The time draws ever closer to the start up of the various CRI units. This will be a time of dramatic change from the system we all grew up with and with which we have come to feel comfortable.

As a group, Chemists will be greatly affected by this change and as I travel around, it is evident that most scientists feel a degree of apprehension about this new system about to be thrust upon us.

A meeting was held in the Beehive in mid December between The Honourable Simon Upton, myself, Alan Turner and representatives of MoRST. The purpose was to explain the NZIC to the Minister, to explore ways in which we can assist in Science and Technology planning and also to present Institute concerns including strong representations on CRI matters.

The Minister is pleased that Chemistry issues should be represented to his department by NZIC and agrees that the appropriate contacts are the President, Science Policy and Public Affairs Committee and the Executive Officer. Through these people we can have direct input on issues such as Chemical Education, Salary/Career structures, Technology transfer, Restructuring of Science Policy, Welfare, Industrial Contacts, Lobbying on behalf of Chemists, etc. Make sure that your local council members are aware of current issues and that they pass these on to our Wellington office. I have planned further visits to the Minister for March to follow up progress and initiatives taken to date.

I am concerned that Chemists can be a bit introverted and so present a conservative image to the public. We must not forget to remind ourselves that life is not all bad and to publicise the many positive aspects of our profession. The SGS Prize for Excellence in Research is a good example of positive attitudes as is the promotion of the Chemical Olympiad for School Students.

I hope that members will make every effort to submit items for Chemistry in N.Z. There were some excellent articles in the December issue and no doubt you are all full of news and views to pass on. It is always good to hear what colleagues are up to.

Branches, I am sure, will "Volunteer" to provide a set of articles for future publications without the need of Presidential persuasion.
Regards
Stan Winter

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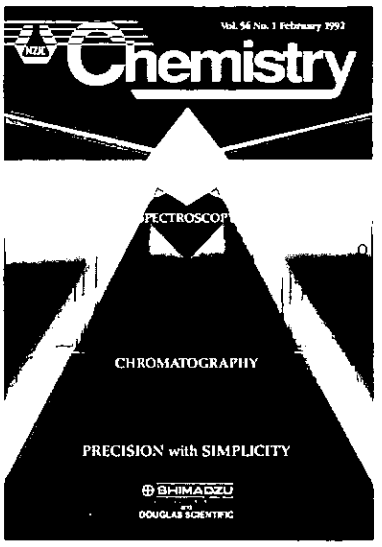

Shimadzu Scientific Instruments are actively represented in New Zealand by Douglas Scientific, a division of Douglas Pharmaceuticals Ltd.

The front cover spectroscopic and chromatographic images depict two traditional areas of leadership in technological innovation and product strength for Shimadzu as the large number of installed spectrophotometers and gas and liquid chromatographs in this country well testify.

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NUCLEAR MAGNETIC RESONANCE — BECOMING PART OF THE MAINSTREAM

by Roger Whiting

After many years of being an organic chemists technique Nuclear Magnetic Resonance has become a powerful tool in a wide range of fields.

INSTRUMENTS GREAT AND SMALL

The field of nuclear magnetic resonance has traditionally been one in which large instruments have dominated. These were housed in special facilities and to run them had their own staff (whose main interest seemed to be the arcane intricacies of Nuclear magnetic resonance). This approach is starting to change as bench top models such as the Bruker Minispec pc 100 become available and applications of the technique are found in a wider variety of industries. These applications are now routine in for example the food industry where nuclear magnetic resonance has proved a rapid sensitive and reliable method for the determination of fats oils and moisture.

The large instruments however still dominate the development of new applications because of the high magnetic field requirements and complex signal generation procedure needed. Thus such instruments as the Hitachi R-series and the Bruker AC and AMX series are all stand alone instruments. For most institutions the acquisition of an nuclear magnetic resonance spectrophotometer represents a major investment.

SOFTWARE DEVELOPMENTS

In nuclear magnetic resonance as in many areas of chemical instrumentation software has been one of the key areas to develop. Bruker have now produced the UXNMR/P for data processing on UNIX based work stations in networked laboratories. This package has a wide range of processing functions including 1 and 2 dimensional plotting and customisable menus. It requires 16MB of memory and 40MB of disk space for full operation. For laboratories operating with a PC environment Bruker have produce 2D WIN-NMR package designed for display of 2 dimensional nuclear magnetic resonance spectra. The requirements for this system are a 286 or 386 processor, 4MB of memory, a VGA graphics adapter and MS-DOS 3.3 (or higher) with Windows 3.0.

2-DIMENSIONAL CORRELATION SPECTROSCOPY (2D COSY)[1]

This technique has proved to be a major advance in Nuclear Magnetic Resonance investigation of complex mixtures. Two dimensional Nuclear Magnetic Resonance spectroscopy can be defined using the following time domains: preparation, evolution (t_1), mixing and acquisition (t_2). One dimensional nuclear magnetic resonance spectra are obtained when the evolution and mixing times are zero. In 2-dimensional nuclear magnetic resonance the evolution and mixing period is used to allow the interacting nuclei to exchange spin energy. The second dimension is generated by sampling this interaction as a function of time in exactly incremented times, t_1. Fourier transformation in both time domains (t_1 and t_2) then gives a 2-dimensional spectrum. The requirement for meaningful 2-dimensional spectra is that the nuclei of interest must interact together in some way.

Correlation spectroscopy (COSY) is a 2-dimensional experiment that relies on the spin — spin coupling between two nuclei. Figure 1 is a typical 2D COSY spectrum. On the diagonal lie the 1-dimensional resonances of a normal Nuclear Magnetic Resonance spectrum while the off diagonal cross peaks indicate groups which are strongly spin coupled together. These of diagonal cross peaks enable certain compounds to be clearly identified in complex mixtures.

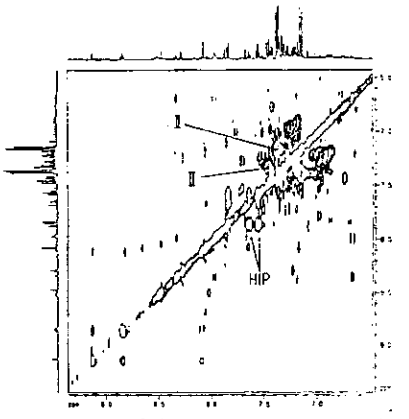

Figure 1. Expansion of the aromatic region of a 2D correlation experiment on a urine sample showing several paracetamol metabolites.

Medical and Biochemical Applications

One of the most exciting applications of the 2D COSY spectrum is in the identification of malignant tumours via detection of a Malignancy — Associated Lipoprotein[2]. Early attempts to identify malignancy of tumours were based on the line shapes of parts of the nuclear magnetic resonance spectrum of the patient's plasma. This was the basis of the Fossel test which has been shown to be unreliable. However, from this came the demonstration of the existence of a malignancy — associated lipoprotein which was investigated using nuclear magnetic resonance. This lipoprotein gave a one dimensional nuclear magnetic resonance peak at 1.34ppm which unfortunately overlapped with peaks from normal samples. Using two dimensional correlation spectroscopy to resolve the overlapping peaks enabled the malignancy associated lipoprotein to be identified. Thus the 2D COSY spectrum of patients serum can display features which appear to correlate with tumour malignancy. Clearly this represent an advance as patient treatment can be planned more precisely before surgery takes place if the metastatic potential of the tumour is known in advance. Further developments of this technique would appear to be heading towards the evolution of equipment to allow a two nuclear magnetic resonance spectrum of a tumour to be obtained from an in vivo scan.

In biochemistry 2D correlation spectroscopy has has been used to identify a range of components in a mixture such as sugars, acids and esters in wine[3]. The technique has also found applications in the elucidation of peptide structures. This is done by consideration of the correlations between C-13 and N-15 nuclei[4].

SOLID SAMPLES

In the solid state nuclear magnetic resonance is hampered by line broadening due to a variety of nuclear spin interactions (mainly chemical shift anisotropy, dipolar and quadrupolar interactions) which are averaged out in liquids. Over the last ten years however there have been significant advances in the development of techniques for nuclear magnetic resonance of solids. These techniques include magic angle spinning, high powered dipolar decoupling, cross polarization and the application of multiple pulse sequences. These are now standard techniques available on the larger instruments and are finding applications in a variety of fields.

Polymer samples

One of the biggest developments in nuclear magnetic resonance of solids over recent years has been the investigation of of polymers. This can be done using H-1 and C-13 as the probe nuclei. The advantage of using C-13 is that it is very sensitive to the conformation of the polymer chain[5]. This counteracts the disadvantage of the its low natural abundance.

Using Magic Angle Spinning Nuclear magnetic resonance it is possible to study the changes occurring in the polymer material at the glass transition temperature by the disappearance of the signals from the chains as the material warms up. Above the glass transition temperature the polymers tend to show narrower bands, typical of liquid samples, due to more rapid molecular motion. Other areas investigated using nuclear magnetic resonance have been the measurement of residual epoxide in epoxy resins. The appearance or otherwise of the carbon peak for the carbon in the epoxide group gives an indication of the residual epoxide in the solid material. This method has the advantage that the measurement is carried out on the solid with out attempting to dissolve the sample which could cause the epoxide to react. Magic angle spinning nuclear magnetic resonance spectroscopy has also been used to investigate the elastomer components in polymer blends. For block copolymers containing butadiene blocks the glass transition temperature of the butadiene is well below room temperature so the peaks from the butadiene appear sharp against the broader matrix peaks. The spectrum can be enhanced by application of multiple pulse sequences.

Inorganic Compounds

The initial application of nuclear magnetic resonance to inorganic chemistry was confined to the use of protons as the probe nucleus and the study of compounds soluble in deuterated solvents. This made it a valuable tool in elucidation of the the structures of organometallic compounds but left the vast range of insoluble inorganic material untouched. However the recent application of the magic angle spinning and cross polarisation nuclear magnetic resonance techniques to inorganic chemistry has contributed to our understanding of the chemistry of a variety of minerals.

The high isotopic abundance of Al-27 and Si-29 has encouraged the investigation of the structures of a range of silicates and aluminosilicates using these as probe nuclei. From the spectrum the nature of the chemical environment of silicon and Aluminium atoms in the mineral can be elucidated [6,7]. This has contributed to our understanding of the processes involved in firing of ceramics. The technique has great promise as there are a wide variety of atoms that can be detected using this technique eg Li-7, Be-9, B-11, C-13, N-14,15, Na-23, P-31, Ga-69,71, Ge-73, Cs-133, Tl-205, Pb-207. In the case of Zeolites there is also the possibility of detecting and investigating the reaction intermediates involved in various catalytic processes.

LIQUID CHROMATOGRAPHY NUCLEAR MAGNETIC RESONANCE DETECTOR

It is axiomatic in the chromatography industry that when a method of detecting compounds is developed it is grafted onto a chromatograph. So Bruker have developed a flow through Nuclear Magnetic Resonance detector for Liquid Chromatography. This can operate in a stopped or continuous flow mode. The advantage that this detector gives to liquid chromatography is the ability to differentiate between different compounds which are eluted from the column at the same time[8].

CONCLUSION

The development of Nuclear magnetic resonance spectroscopy is providing ever more powerful techniques for investigating a widening range of materials. The appearance of smaller, cheaper routine instruments will also encourage the use of the technique in a number of industries which will no doubt encourage users to tackle a broader spectrum of problems using nuclear magnetic resonance.

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STRONG SUPPORT NEEDED FOR THE NEW ZEALAND CHEMICAL OLYMPIAD TEAM

CHEMICAL OLYMPIAD PROJECT — PROGRESS REPORT

Since my attendance at the 23rd International Chemical Olympiad held in Lodz, Poland in July, 1991, a number of things have occurred that should lead to a New Zealand team competing for the first time in Pittsburgh in July, 1992:

1) On 31 October, 1991 ninety students from forty one schools sat a training group selection examination to select a training group of 20 students. The standard of students entered was very high. Offers to join the group went to students spread from Invercargill to Auckland.

2) New Zealand received an official invitation to come from the 24th IChO Planning Group and the American Chemical Society.

3) Work has commenced on organising the training program which will occur during first term. This will involve weekly assignments, and where possible, contact with university mentors.

4) Fund raising has begun. In these hard economic times many companies are unwilling to support activities such as this. However it is felt that, with perhaps some modification of the training program, we will be able to send a full team to the U.S.A.

We acknowledge support from the following organisations, which has been received to date: Dynavac New Zealand, Fay Richwhite, John Ilott Charitable Trust, the committee of "Chemical Processes in New Zealand" McGraw-Hill Book Company New Zealand Limited, Mobil Oil New Zealand Limited, New Zealand Institute of Chemistry, New Zealand Refining Company Ltd, Rohm and Haas N.Z. Ltd, Thermoplastic Engineering Limited, and Union Carbide Chemicals (N.Z.).

Robert Maclagan

CHEMICAL OLYMPIAD — A message from the Institute Vice-President

In 1991 the Institute supported Dr. Maclagan's attendance at the Chemical Olympiad in Poland as an observer in preparation for a possible participation by N.Z. school pupils in 1992. Dr. Maclagan returned from the 1991 experience convinced that we should indeed take part in the 1992 event and it is largely due to his enthusiasm and hard work that we have already gone as far as conducting the selection examinations for a group of 20 pupils who will participate in the training camp in May of this year.

I have two main reasons for supporting our involvement in the Olympiad. First it provides an opportunity for four talented young New Zealand chemists to pit their wits and skills against those of other enthusiasts from all over the world. Second and more importantly it provides an opportunity for many more youngsters and for teachers throughout New Zealand to get some fun out of a friendly competition.

Too often we hear that competitive examinations are bad and that they foster a sense of failure. We seem to have no such inhibitions in the field of the physical sports and I see no reason why pupils who enjoy chemistry and excel at it should not have the opportunity to develop and to demonstrate their excellence.

The initial budget for the operation — preliminary exams, training camp and attendance at the Olympiad proper — came to about $28,000. The Institute has committed a couple of thousand dollars towards this cost. Teachers have already given time and effort to the preparation of their pupils for the examinations and some will make a further contribution in helping to run the training camp in May. Many pupils have worked hard in preparing for the preliminary exams, those who attend the camp will have an enjoyable and hard working experience and the final four will have the excitement of travelling to Pittsburgh and attending the Olympiad itself.

While you may regard the Institute's contribution to the Olympiad costs as appropriate recognition by the profession as a whole of its worth there will be other members who feel, as I do, that this is a project which deserves a strong individual statement of support and is one to which you would want to make a more direct personal contribution. I appeal to members who do feel this way to join me in sending their personal contribution to:

Chemical Olympiad Project, C/- Alan Turner, N.Z.I.C., P.O. Box 12-347, Wellington.

A.G. Williamson, Vice President

SOIL WATER CHEMISTRY AND MINERAL STABILITY IN SOILS

A PHYSICAL CHEMISTRY APPROACH

PRESIDENTS ADDRESS TO NZIC BRANCHES 1991

by Harry Percival
DSIR Land Resources Lower Hutt

Weathering of rocks into soil minerals

Soil is a complex mixture of inorganic and organic compounds containing, for example, mineral materials, organic matter, water and air. Figure 1 illustrates the development of well developed soil from fresh rock over time. The mineral materials component is a loose mass of broken and chemically weathered rock and of interest here is its interaction with soil water which contains a variety of chemical elements in solution (such as potassium, calcium, chloride, sulphate *et al*).

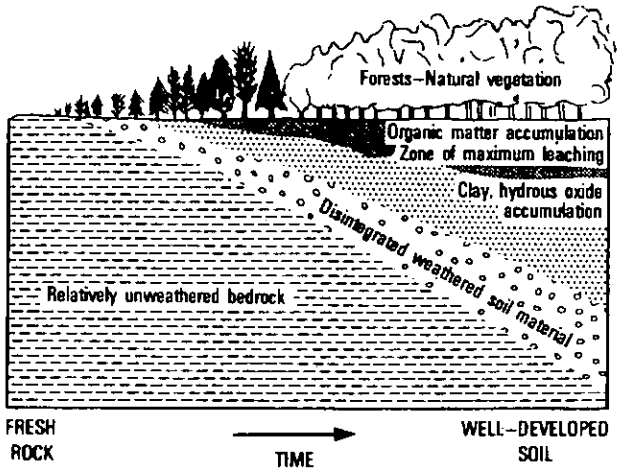

Figure 1: Soil profile developed from weathering (in place) of rock [adapted from Brady (1984)].

The weathering of rocks to form soil is essentially a combination of the mechanical process of disintegration where rocks and minerals are reduced in size and the chemical process of decomposition of minerals within rocks that are caused by hydrolysis, i.e. reaction of minerals with water, and other chemical effects such as oxidation. Soluble components from minerals with water, and other chemical effects such as oxidation. Soluble components from minerals are released into the reacting waters and new minerals are synthesised or are left as resistant end products. The overall scheme of weathering processes under conditions common in humid temperate regions like New Zealand are illustrated in Figue 2. It illustrates

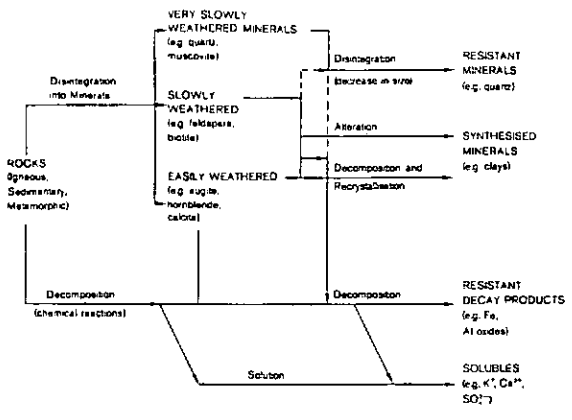

Figure 2: Weathering pathways under acidic conditions [after Brady (1984)] (solid lines represent major pathways, broken lines minor pathways).

that the inorganic fraction of the soil comprises the residual weathering products of rocks and minerals as the more soluble components are leached away by water.

Why should rocks weather as they do to form soils? Chemical weathering of rocks occur because the rocks which emerge at the surface of the earth, after having been formed at different temperatures and pressures within the earth, are not in chemical equilibrium with present surface conditions, i.e. primary rock-forming minerals are usually unstable in the presence of water at ambient temperatures and one atmosphere pressure. These primary minerals weather to secondary minerals of greater stability under earth-surface conditions, viz clays and associated minerals. Figure 3 lists the more important original or primary minerals and the secondary minerals derived from them. The production of new minerals by chemical weathering depends on the nature of the primary minerals present in the rocks and their chemical environment as represented in Figure 4.

ORIGINAL MINERALS		SECONDARY MINERALS	
Quartz	SiO_2	Clay minerals	Al Silicates
Microcline	$KAlSi_3O_8$*	Gibbsite	$Al(OH)_3$
Orthoclase		Haematite	Fe_2O_3
Na plagioclase	$NaAlSi_3O_8$*	Limonite	$Fe_2O_3.3H_2O$
Ca plagioclase	$CaAl_2Si_2O_8$	Calcite	$CaCO_3$
Muscovite	$KAl_2Si_3O_{10}(OH)_2$	Dolomite	$CaCO_3.MgCO_3$
Biotite	$KAlMg_2Fe_2Si_3O_{10}(OH)_2$	Gypsum	$CaSO_4.2H_2O$
Hornblende	$Ca_2Al_2Mg_2Fe_2Si_8O_{22}(OH)_2$	Apatite	$Ca_5(PO)_3.(Cl,F)$
Augite	$Ca_2(Al,Fe)_4(Mg,Fe)_4Si_8O_{24}$		

*Formula also that for Volcanic K or Na-Glass

Figure 3: The more important original (primary) and secondary minerals in soils [adapted from Brady (1984)].

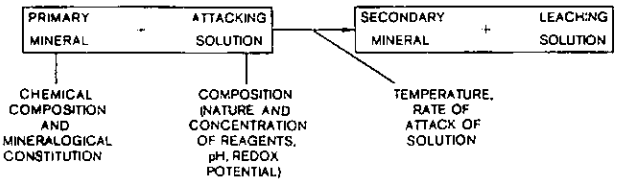

Figure 4: Schematic representation of chemical weathering [after Pedro and Siefferman (1979)].

Interactions between minerals and aqueous solutions — application of stability diagrams

Chemical weathering environments of waters in contact with minerals can be represented by their chemical composition such as concentrations of cations (e.g.K^+, Ca^{2+}), anions (e.g.Cl^-, SO_4^{2-}), aluminium ions, soluble silicon, and pH. It can be shown that minerals which are the least soluble in a given aqueous environment are also the most stable while the most soluble minerals are the least stable. Therefore knowing the chemical composition of waters in contact with minerals (say, the soil waters in between soil particles or interstitial waters in rocks) provides a tool for predicting the stable mineral or minerals in a given environment when mineral solubilities are known. We can identify those minerals which will precipitate or persist in a given soil/rock system or those that will dissolve or cannot persist.

If we wish to determine the relative stabilities of minerals under specific weathering environments (i.e. related to specific composition of contact waters) then a very good way of doing this is to construct stability diagrams showing the solubility relationships of the minerals in question. We do this by graphing equations describing the most suitable solubility reactions for the minerals in an eqeous (weathering) environment under

equilibrium conditions. We must also know the equilibrium constants of the solubility reactions.

$SiO_2 + 2H_2O$ (quartz)	⇌	$H_4SiO_4^0$
$KAlSi_3O_8 + 4H^+ + 4H_2O$ (microcline)	⇌	$K^+ + Al^{3+} + 3H_4SiO_4^0$
$Al_2Si_2O_5(OH)_4 + 6H^+$ (kaolinite)	⇌	$2Al^{3+} + 2H_4SiO_4^0 + H_2O$
$Al(OH)_3 + 3H^+$ (gibbsite)	⇌	$Al^{3+} + 3H_2O$

Figure 5: Equilibria: minerals-aqueous solution.

Figure 5 shows the solubility reactions for four selected minerals-quartz, and microcline (examples of primary minerals), kaolinite and gibbsite (examples of secondary minerals). These reactions are written in a form where all the constituent elements (Si, Al, K) in the minerals are in soluble form in the solubility reaction products. Soluble silicon is represented by the neutral species, $H_4SiO_4^0$. The equilibrium constant relation that applies to the equilibrium reactions in Figure 5 is illustrated with kaolinite in Figure 6 [(kaolinite) and (H_2O) have unit activities].

$$K^0 = \frac{\text{Product of Activities of Reaction Products}}{\text{Product of Activities of Reactants}}$$

$$K^0 \text{ (kaolinite)} = \frac{(Al^{3+})^2(H_4SiO_4^0)^2(H_2O)}{(\text{kaolinite})\,(H^+)^6}$$

$$\log K^0 \text{ (kaolinite)} = 2 \log (Al^{3+}) + 2 \log (H_4SiO_4^0) + 6\ pH$$

Figure 6: Equilibrium constant relation for mineral dissolution reactions.

Figure 7 shows the results for all the minerals considered here. The log values of the chemical species on the right-hand side of the equation are logs of the thermodynamic activities of the named species. Thermodynamic activities are the "effective" concentrations in solution of the species, and are related to their actual concentrations. Algebraic rearrangement of the equilibrium constant equations into the linear equation form shown in Figure 8 allows us to represent the solubility reactions graphically by plotting the ($\log Al^{3+} + 3\ pH$) variable against $\log H_4SiO_4^0$ for given values of $\log K^+$ and pH, and the known values of $\log K^0$. Such plots form a stability diagram (or solution composition diagram) in which the stabilities of minerals can be compared under given environmental conditions.

We can begin with the stability diagram in Figure 9 showing a selection of primary minerals and compare their solubility relationships with each other and with gibbsite, a 'reference' secondary mineral often formed at the end of the weathering

Quartz	$\log K^0$	=	$\log H_4SiO_4^0$
Microcline	$\log K^0$	=	$\log K^+ + \log Al^{3+} + 3 \log H_4SiO_4^0 + 4\ pH$
Kaolinite	$\log K^0$	=	$2 \log Al^{3+} + 2 \log H_4SiO_4^0 + 6\ pH$
Gibbsite	$\log K^0$	=	$\log Al^{3+} + 3\ pH$

Figure 7: Equilibrium relations for mineral-solution interactions.

Quartz*	$\log H_4SiO_4^0$	=	$\log K^0$
Microcline	$\log Al^{3+} + 3\ pH$	=	$-3 \log H_4SiO_4^0 - \log K^+ - pH + \log K^0$
Kaolinite	$\log Al^{3+} + 3\ pH$	=	$-\log H_4SiO_4^0 + 0.5 \log K^0$
Gibbsite	$\log Al^{3+} + 3\ pH$	=	$\log K^0$

*line vertical to x-axis at value of $\log K^0$.

Figure 8: Line equations for ($\log Al^{3+} + 3\ pH$) vs $\log H_4SiO_4^0$ stability diagrams.

sequence for soil minerals. This stability diagram has been drawn for the conditions: 25°C, 1 atmosphere pressure, pH=7 and $\log K^+ = -3$ (i.e. K^+ activity = 10^{-3} M, a common value in soil waters) with $\log K^0$ values taken from Lindsay (1979). Two of the minerals for which solubility line equations were developed (in Figure 8) are included — microcline and gibbsite. The other minerals are muscovite and K-glass (derived from volcanic ash) — the fomulae of which are given in Figure 3. With other specified environmental conditions the solubility can shift position in the diagram and also relative to each other.

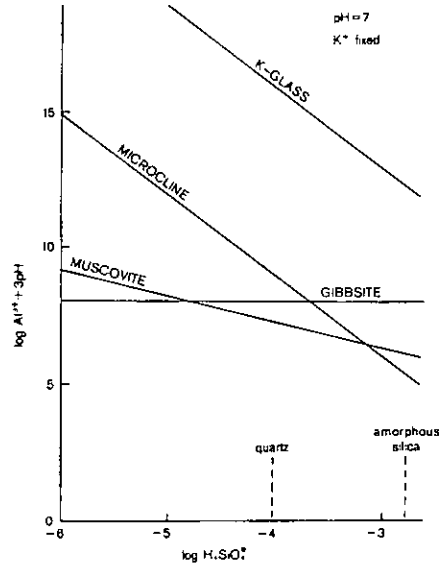

Figure 9: Stability of representative primary minerals compared to that of gibbsite.

Considerable information can be extracted from this type of stability diagram. In such diagrams each line represents the equilibrium solubility of a mineral, as shown, and the most stable mineral at a given soluble silicon activity is the one whose line at that point is the lowest in the diagram. This is the least soluble mineral at that point. Other minerals whose solubility lines lie progressively higher in the digram at that point are less and less stable. Therefore, we obtain a hierarchy of stability. Under the aqueous conditions specified for this diagram the order of stability of the minerals shown will vary with activity of the soluble silicon. At low silicon activities the order of decreasing stability is gibbsite, muscovite, microcline, and K-glass; while at high silicon activities the order changes to microcline, muscovite, gibbsite, K-glass. At in-between silicon activities muscovite is the most stable mineral. K-glass is clearly the least stable of the group of minerals shown at all silicon activities and would be the most weatherable mineral under the specified aqueous conditions.

Where solubility lines cross in the stability diagram both minerals represented by those lines can coexist, i.e. the crossing points represent the situation where both minerals are in equilibrium with each other as well as with the contacting water. Again, the most stable mineral 'pairings' are those at the lowest points in the digram viz. muscovite/gibbsite at a low silicon activity and muscovite/microcline at a high silicon activity. The microcline/gibbsite pair are less stable than muscovite at the silicon activity represented by the crossing point.

What else can the stability diagram tell us? If we take, for example, a soil water composition whose pH, Al^{3+}, and soluble silicon level is such as to place it in the diagram below the solubility line of a particular mineral then the soil water is undersaturated with respect to that mineral, i.e. the mineral will tend to dissolve. Alternatively, a composition position above a solubility line of a particular mineral means that the soil water is supersaturated with respect to that mineral, i.e. the mineral will tend to precipitate. This all means that the minerals in contact with the soil water will tend to be those that are the least soluble (most stable) at the given soil water composition.

It is not uncommon to find minerals present in a soil that are (thermodynamically) unstable under the prevailing soil water composition. These minerals are termed 'metastable' minerals

and will ultimately convert to stable minerals appropriate to the soil water composition. However, the conversion rate may be very slow.

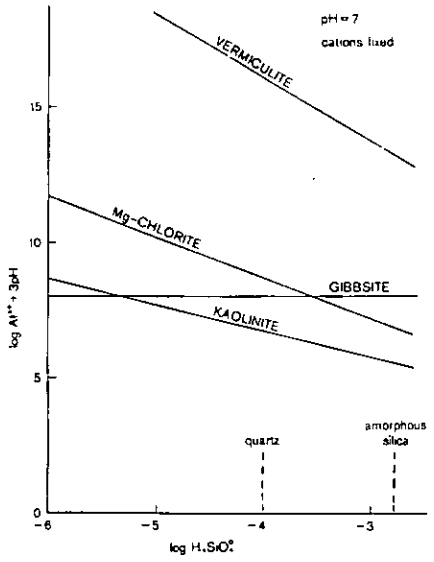

Figure 10: Stability relations of representative secondary minerals.

We have had a look at a stability diagram containing mainly primary minerals. Figure 10 shows the corresponding diagram for a set of secondary minerals (formed under earth surface conditions as against crustal conditions for primary minerals, with gibbsite again acting as a 'reference' mineral. This stability diagram has been constructed for conditions similar to that for the primary mineral example shown earlier, i.e. for pH=7 and fixed levels of activities for the cations associated with Mg-chlorite, $Mg_5Al_2Si_3O_{10}(OH)_8$ and vermiculite, $[Mg_{2.71}Fe(II)_{0.02}Fe(III)_{0.46}Ca_{0.06}K_{0.1}]Si_{2.91}Al_{1.14}O_{10}(OH)_2$. log K^0 values were again taken from Lindsay (1979). The diagram shows that at low soluble silicon activities the order of decreasing stability is gibbsite, kaolinite, Mg-chlorite, and vermiculite; while at high silicon activities the order changes to kaolinite, Mg-chlorite, gibbsite, and vermiculite. Vermiculite is always the least stable of these minerals under the specified aqueous conditions. Vermiculite is actually not uncommon in soils, but it exists as a metastable phase. In general the tendency in most aqueous environments in soil systems is for primary minerals to give way to secondary minerals of greater stability (however, 'metastable' intermediate minerals may be found on the way). Stability diagrams of the type shown makes one appreciate that a variety of minerals can be formed in soils in response to a variety of soil water environments and that the chemical weathering environment can be quantified.

Relative stabilities of some aluminosilicates important in NZ soils

Now that I have briefly discussed the stability sequences of primary and secondary minerals in general I want to concentrate for a short time on a suite of aluminosilicate clay minerals that are significant in many New Zealand soils. There are the minerals kaolinite, halloysite, imogolite, and allophane. The equilibrium solubility reactions are shown in Figure 11. The derived equations for plotting the solubility lines in a stability diagram are shown in Figure 12 obtained by following the equilibrium constant relation procedure described earlier. Figure 13 shows

$Al_2Si_2O_5(OH)_4$ (kaolinite, halloysite)	$+ 6\ H^+ \rightharpoonup 2\ Al^{3+} + 2\ H_4SiO_4^0 + H_2O$
$Al_2SiO_3(OH)_4$ (imogolite)	$+ 6\ H^+ \rightharpoonup 2\ Al^{3+} + H_4SiO_4^0 + H_2O$
$Al_4Si_2O_5(OH)_{10}$ (allophane)	$+ 12\ H^+ \rightharpoonup 4\ Al^{3+} + 2\ H_4SiO_4^0 + 7\ H_2O$

Figure 11: Equilibria: minerals-aqueous solution (for some minerals significant in New Zealand soils).

Kaolinite, Halloysite	$\log Al^{3+} + 3\ pH =$	$- \log H_4SiO_4^0 + 0.5 \log K^0$
Imogolite	$\log Al^{3+} + 3\ pH =$	$- 0.5 \log H_4SiO_4^0 + 0.5 \log K^0$
Allophane	$\log Al^{3+} + 3\ pH =$	$- 0.5 \log H_4SiO_4^0 + 0.25 \log K^0$

Figure 12: Stability line equations for the minerals in Figure 11.

the stability diagram containing the solubility lines for kaolinite, halloysite, and imogolite compared to that of gibbsite. [The log K^0 values (25°C, 1 bar pressure) used for this stability diagram were 8.04 (gibbsite), 6.68 (kaolinite), 8.86 (halloysite), 12.08 (imogolite), -4.00 (quartz), and -2.71 (amorphous silica), taken from the author's unpublished review of equilibrium constants which is currently being updated for publication]. There are currently no reliable solubility data available for allophane so no solubility line is drawn for that mineral. I will discuss allophane again shortly.

This stability diagram holds for any pH value (in the normal range of 4-9 for soils). It shows that over a very wide range of soluble silicon activities kaolinite is always the least soluble, and therefore most stable, mineral relative to halloysite and imogolite (and to gibbsite except at very low silicon activities). Therefore the tendency will be for halloysite and imogolite to dissolve and for kaolinite to be precipitated. The presence of halloysite and imogolite in soils suggests that the kinetics of precipitation of these minerals is much more rapid than that of kaolinite or gibbsite otherwise halloysite or imogolite would never form in soils. Therefore both halloysite and imogolite can be regarded as fast-forming 'metastable' minerals.

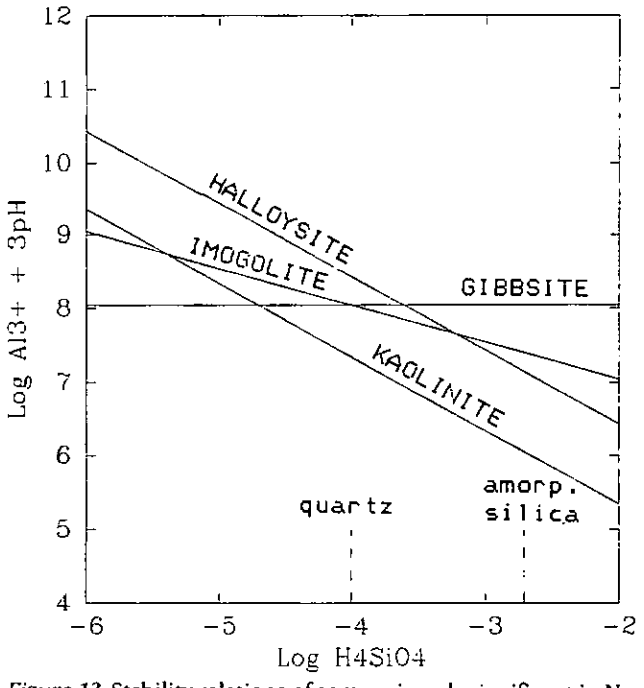

Figure 13: Stability relations of some minerals significant in New Zealand soils.

The stability diagram shows that, in the absence of kaolinite, imogolite is more stable than halloysite at silicon activities of less than about 15 ppm (at ≤3ppm silicon gibbsite becomes the most stable). This implies that under environmental conditions in soils where soluble silicon is removed from soils by moderately intense leaching halloysite could (theoretically) dissolve and imogolite be precipitated. I will show the practical consequences of this stability shift shortly.

Where does allophane fit into the stability sequence of the aluminosilicate clay minerals being discussed? Allophane is known to have a variable composition, in particular variable Si/Al ratios in its structure so that, for example, allophanes possessing ratios of 1/2 and 1/1 are both known. The 1/2 allophane is the most common type of allophane in New Zealand soils. A 1/2 allophane has the same Si/Al ratio as imogolite (and indeed this

allophane is usually referred to as proto-imogolite allophane because of its close structural and chemical formula relationship) while a 1/1 allophane has the same Si/Al ratio as halloysite (and kaolinite). In a stability diagram of the type shown here solubility lines for minerals containing the same Si/Al ratio always lie parallel to one another. Therefore solubility lines for 1/2 allophane and 1/1 allophane would lie parallel to those of imogolite and halloysite respectively. They would lie above or below the solubility lines of these two latter minerals if they were less or more stable respectively. However to fix the positions of the solubility lines of the 1/2 and 1/1 allophanes we would need to know the equilibrium constants of their solubility reactions. To date these have not been experimentally determined, perhaps because of the variable composition of allophanes. However, we can surmise that the 1/2 allophane (proto-imogolite allophane) will probably be very similar in stability to imogolite and to this extent imogolite can act as a 'model' for 1/2 allophane in stability diagrams, in the absence of equilibrium solubility data for allophane.

A case study of mineralogical change in relation to soil water chemistry

The imogolite 'model' of allophane stability has proved to be useful in interpreting recent field observations of a sequence of soils in which allophane has tended to give way to halloysite as the dominant aluminosilicate clay mineral depending on the drainage conditions for the soils. The mineral stability diagram approach gives us a way of explaining this. The soil profiles (vertical sections of soils) chosen for study were located in the Waikato near Hamilton, viz profiles of Horotiu, Bruntwood, and Te Kowhai soils. These soils are quite close together physically, a matter of tens of metres (rather than hundreds), subject to the same climatic factors and parent rocks but differing in drainage patterns. Figure 14 gives some details about these profiles, concentrating on the subsoil horizons which are low in organic carbon and biological activity and which therefore are dominated by inorganic chemical processes.

Soil	Depth (cm)	Clay Mineralogy includes
Horotiu silt loam	31-130 (5 horizons)	Allophane and kaolin. Dominated by allophane.
Bruntwood silt loam	24-105 (5 horizons)	Allophane and halloysite. Dominated by allophane to 67 cm, thereafter by halloysite
Te Kowhai silt loam	32-128 (8 horizons)	Halloysite. No allophane

Figure 14: Major mineralogical features of soils varying in drainage characteristics.

Soil waters were extracted from the various horizons of field-moist soil samples by the method outlined in Figure 15 viz by centrifuging the samples with a dense water-immiscible organic liquid to displace the aqueous solution from between the soil particles. The aqueous solution forms a layer over the organic liquid, is separated from the organic liquid and then microfiltered to provide a particle-free solution for chemical analysis (Percival, 1990a). Chemical analyses of the soil waters are carried out for the species shown in Figure 16 (ion chromatography can also be used to measure the concentrations of the anions listed). The resulting data was processed (Percival, 1990b) using the computer programme GEOCHEM (Sposito and Mattigod, 1980) to calculate the equilibrium distribution of solution species, particularly that of the inorganic aluminium species Al^{3+} which is required data for stability diagrams involving aluminosilicate minerals.

(1)	CENTRIFUGING	
	Sample:	150 g field-moist soil
	Displacent:	Arklone P (a trifluoroethane) or 1,1,1-trichloroethane
	Containers:	250 ml Polypropylene, or 300 ml stainless steel
	Centrifuge:	11,000 rpm for 30 min
(2)	PHASE SEPARATION (IPS Whatman Paper)	
(3)	MICROFILTRATION	
	Membrane:	0.2 μ cellulose nitrate
	Apparatus:	Plastic Millipore

Figure 15: Conditions for soil solution extractions by the immiscible displacement technique.

Determination	Method
pH	pH meter
Soluble silica	Spectrophotometry
Cations:	
Na, K, Ca, Mg, Fe, Mn	Atomic Absorption
NH_4^+	Auto analysis
Al	Spectrophotometry
Anions:	
Cl^-	Spectrophotometry
F^-	Spectrophotometry
HCO_3^-	Auto titration
NO_3^-	Auto analysis
SO_4^{2-}	Auto analysis
PO_4^{3-}	Auto analysis

Figure 16: Analysis of soil solution constituents.

The Horotiu silt loam is a well drained soil whereas the Te Kowhai silt loam is poorly drained throughout the profile. Intermediate between these two soils is the Bruntwood silt loam where the upper horizons are well-drained but the lower horizons are poorly drained. In this particular soil sequence allophane (1/2 Si/Al) is the dominant clay mineral in the well drained portions of the profiles and halloysite is dominant in the poorly drained portions. It turns out that the driving force, if you like, for this distinctive change in aluminosilicate mineralogy is the relative stabilities of allophane and halloysite under the different chemical weathering environments imposed by the different drainage conditions. The drainage conditions have influenced the soil water compositions in contact with the soil minerals, which in turn have caused soil mineral/solution reactions to shift in favour of the more stable mineral in the conditions. This can be illustrated by reference to Figure 17 which shows soil water compositions for the various horizons in the Horotiu, Bruntwood, and Te Kowhai profiles plotted on the

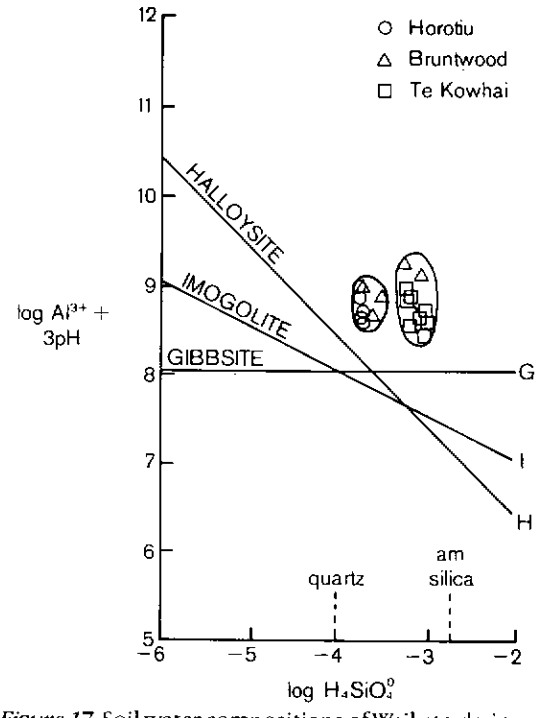

Figure 17: Soil water compositions of Waikato drainage sequence soils compared with solubility lines of the dominant minerals in the soil profiles.

stability diagram containing the minerals, gibbsite, imogolite, and halloysite.

Data falls into two main groups with respective soil water silicon levels of about 6 ppm (mg/l) and about 23 ppm (mg/l). [The log scale in the diagram makes the two groups of points look closer together than in fact they are-they are very significantly different groups]. Now the 6 ppm silicon group of points are those representing the well drained horizons of the Horotiu soil profile (all horizons) and the Bruntwood profile (upper horizons) in which soluble silicon has leached out of. Conversely, the 23 ppm silicon group of points are those representing the poorly drained horizons of the Bruntwood profile (lower horizons) and the Te Kowhai profile (all horizons). Thus, the 6 ppm group plot in the area of the stability diagram where imogolite (which can be taken as representing 1/2 allophane) is the more stable of the two minerals imogolite (allophane) and halloysite, whereas the 23 ppm group plot where halloysite is the more stable. This accords well with the mineralogical observations of allophane dominance in the horizons corresponding to the 6 ppm silicon group and halloysite dominance in those horizons corresponding to the 23 ppm group.

What we are seeing here is the dominant alumino-silicate clay mineralogy being controlled by the soil water silicon level, which in turn is being influenced by the drainage characteristics of the soil profiles. So that, when the silicon level is less than about 15 ppm allophane will predominate over halloysite and when greater than about 15 ppm the reverse is likely to occur in soils where these minerals are present. This is a good example of the explanatory power of the stability diagram approach to explain observational data on mineralogy and the soil water composition associated with the mineralogy.

A. Labile, monomeric species -
   Al^{3+}
   Al-OH (hydroxide complexes)
   Al-SO_4 (sulphate complexes)
   Al-F (fluoride complexes)

B. Non-labile monomeric species -
   Al-organic complexes

C. Acid-soluble species -
   Strong Al-organic complexes
   Polymeric compounds
   Colloidal particles
   Adsorbed Al on colloidal particles, or on large organic molecules

Figure 18: Aluminium species in natural waters.

The complexity of aluminium chemistry in waters

Before I leave this subject I want to briefly discuss two interesting complicating factor in interpretation exercises of the type I have been describing. This is also an area of current and future research.

In the stability diagrams we have been looking at the aqueous species of aluminium used as the 'reference' is Al^{3+}, i.e., the Al^{3+} activity must be known or be calculable from measurements of total aluminium to be able to use the diagrams for interpretation of soil water composition. Soil waters will contain some or all of the species of aluminium shown in Figure 18. Not included in Figure 18 are the very slowly acid-soluble species of aluminium in clay particles and very fine sand particles. Al^{3+} is always present even if it is only a small proportion of the total aqueous aluminium in the water.

Al^{3+} activity can be calculated from a knowledge of the total aluminium in solution, the pH, total concentrations complexing species of, and the relevant equilibrium constants of the complexing reactions. This can be difficult in practice if there is uncertainty about the actual Al species present and their concentration, particularly the Al-organic complexes which can vary widely. Research is on-going into identifying and measuring these complexes. In addition methods are being developed to measure only specific groups of Al species in the soil water such as the labile, monomeric species (inorganic complexes) or the non-labile, monomeric species (organic complexes). The Al^{3+} activity calculation is most reliably performed when only the group of labile, monomeric species is measured since the inorganic complexes listed in the slide are fairly well characterised.

Conclusion

Finally, the stability diagram approach is not only useful in understanding the formation and weathering of the mineral system in soils. It has a wider application because soil mineral equilibria, by controlling the aqueous concentrations of elements, affect all biogeochemical processes. Therefore applications are possible in the important areas of inorganic waste disposal (including nuclear waste), groundwater contamination by toxic elements, plant nutrition, and geochemical modelling in general; all areas in which the identification of solubility-controlling solids is important.

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Another sample appeared in the tube in front of him. He reacted with a speed appropriate to his age, which was what the young call old and what he called mature.

After all, he reflected, there were no middle-aged people around any more; they were all either at education, learning how to make the automatic equipment that made everything else, or they were at compulsory, paid, leisure-activity, even if that was a conflict of terms.

The young, once they had learnt to read, write and use calculators, did most of the donkey work in the few years they had before they chose their life's work or play. The old (he was not one of course) did most of the non-physical work where decisions and judgements were called for, and where the young could make such expensive mistakes. Mistakes were permitted because progress had to be made in automating production even further, and that was the only way of discovering what refinements could be made. This also served to give the middle-aged some challenges in life. Although he didn't really believe it, it had been said the sheer volume of industrial production was such that if it was all perfect, the world would be swamped by it.

What he had to do was make decisions about testing the sample to prove its suitability for use. In the olden days - as others kept calling them - he would have had to do most of the testing himself, with the help perhaps of colleagues skilled in different disciplines, but now all he had to do was push the buttons on the console in front of him, and the rooms full of automated testing gear would do the rest. The master computer would take over after that and check that the results were consistent with their standards.

He had done similar jobs in drug and cosmetic firms during his lifetime, but they were the old-fashioned non-automatic companies, where most of the production and practically all the laboratory work was done by people. In those days, machines did only the repetitive work, and laboratory gear measured only those intangibles that the human senses could not detect.

The high cost of automation had forced all the smaller companies to amalgamate, although the plant turned out products under many different brands. In some ways this made his job more important because the raw materials had to meet everyone's needs.

The master computer, smaller and more capable of making decisions without specific programming than the superceded mainframe computers, still had some limitations and he was pleased that he had some control, however slight.

One torrid day he had had a particularly nasty argument with the master computer which left him exhausted so he hoped that it would not disagree with what he now decided. He pushed the necessary buttons, typed in an extra instruction and touched the spot marked GO. The sample disappeared without a murmur from the master. It was time for coffee but it was hardly worth moving for, even if the human contact it could bring was desirable. He called up the lounge and saw that no one was there, and a flick of Joe's switch and a few words to Joe's image established that Joe wasn't moving either. He had used his one-hour allocation of visual entertainment so he used music to fill his mind while drinking the coffee he got from his personal dispenser.

Calling his wife was easy but he knew she was usually resting at this hour, and besides, what did he have to say to her?

Coffee over, and a few turns on the exercise machine having refreshed his body, he called up the book he had been reading. Screens were much brighter and clearer than they had been in the days when paper books were first superceded by cassettes, and he could read at his own pace, flick through the "pages" if he wanted or change to an illustrated book, with far less effort than it used to be.

The lack of physical effort was one of the penalties of modern times, he thought, and the delight of finding something he enjoyed in an old-fashioned library would never be experienced by the young. His own collection of books, papers, journals and magazines was a source of amazement and wonder to his grandchildren, but he seldom used it, except to dig up facts he couldn't quite remember, or personal notes he had made.

His reading was interrupted by a gentle alarm sounding on the console, and bringing himself back to reality he saw the sample had reappeared in front of him, and the screen, when he asked what was wrong, said "Results inconsistent with nature of material." 'Good,' he thought, 'the master computer is not so clever after all.' Calling up the results the automatic instruments had obtained confirmed the inconsistency and he wondered what other tests he should get done.

To avoid holding up the machine he pushed the reject control, and the sample fell out in front of him. It was harmless enough, and he had handled it often in the "olden days" when tests were done on a laboratory bench, and he cast his mind back to what could possibly be wrong. He had certainly chosen the right tests, and he trusted the results of the hidden instruments, but there was another factor niggling at the back of his mind. A time for action, he decided, and putting the console on standby, he picked up the sample, got to his feet, and left the room.

Not too many people knew of the existence of the place he was going, because once an automated plant was built there was a strong reluctance to modify it. Tearing it down and building an improved version was more likely, so he had no real fears as he put the key in the lock, went in and locked the door behind him.

A nostalgic wave swept over him as he looked at the familiar objects, and he went over and switched on a hotplate and a stirrer. The beakers, flasks, bottles of chemicals and the two balances brought back memories of a multitude of hours, some happy, some dull, and some just frustrating. Applying himself to the job at hand, he took the sample, weighed out a suitable portion and reached for a book from the shelf.

A rapid titration - and what a delight it was to see the colours changing under his own control - told him part of the answer he wanted. Another reference book, and a glance at some records he had been lucky enough to save, suggested what he should do next. Half an hour went quickly and he made a quick trip back to the console in case there was a backlog. Back at what he called the "real" laboratory, he suddenly realised what the problem was, and made another test. Happy at solving the problem, he tidied up and washed all the glassware carefully, made sure that the room was safe, and whistled his way around the corridors to the multi-buttoned desk.

Replacing the sample in the entry tube, he tapped out the instructions the automatics would need to do the job in the light of what he had found, then dealt with the few samples accumulated while he was away.

The end of his shift was approaching when the master computer flashed him a message "I see we have now passed the rejected sample". "Yes," he tapped back - some people used "confirm" but he always thought that was an Americanism for the shorter word - "I made a personal examination and reset the parameters". "Thank you and congratulations," said the master. It was hard to realise that it was not a human responding to him but he knew that it was in a way a second-hand brain, the result of excellent programming.

He was packing up to go, since his replacement would almost certainly arrive on time, when the master flashed another message at him. "Because of your superior performance I have rearranged the schedules next week so that you can have a day off. Please choose a day". The unusualness of this message startled him at first because it had never happened to him before. Must be a new feature added during the last programming refinement, he thought, and quickly entered "Thursday, thank you." Immediately he saw the foolishness of thanking an electronic device, but it was even sillier to try and correct it. "O.K." came back before he had though this out, anyway.

As he picked up his things the next operator arrived and, heading for the single unit transports, he couldn't help feeling that he worked for a good organisation. Now, what would he do on his day off?

Contributed by C.L.H. Stonyer, after 50 years of non-automated chemistry.

COLOUR: CONCEPTS AND MEASUREMENT

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Colour is a ubiquitous phenomenon and it would be hard to imagine a world without it. The chemistry of substances which give rise to colour is relevant in a variety of scientific disciplines and is of considerable importance in many industries which employ chemists. The manufacture of printing inks, paints, pigments, food colorants, textile dyes, bleaches etc., and international trade in these items is of worldwide commercial significance. Equally important are the numerous industrial processes in which they are used. These all have the common goal of producing particular colours in products, and to do so reproducibly. That goal demands an essential extension of the chemist's knowledge of colorants and coloration processes so as to include an understanding of the nature of colour, its measurement and the specification of colour differences.

The nature of object colour

Colour is something one sees. The visual process responds to light coming from an object and gives rise to the perception of colour in the mind of a human observer. Therefore colour is a psychological phenomenon. From this stems an important corollary, which is that strictly speaking, neither light nor objects possess a property called colour, whatever common sense or experience may suggest to the contrary. This was recognised in 1730 by Sir Isaac Newton [1], and this fundamental fact formed the basis for extensive investigations on colour over subsequent years which lead ultimately to the current system of colour measurement which was established by the Commission International d'Eclairage (CIE)[2].

The specification of colours

Colour information may be acquired and communicated in various ways, but in a scientific context there are requirements for consistency independent of time, distance and language.

Although the average person may be able to distinguish over a million colours, the description of visual observations by the use of general colour terms is the least precise. The range of names upon which people can be relied to agree is very limited, perceived colour depends on the conditions of illumination, different observers may have different colour discrimination and there is no simple way of using visual observations to describe the extent of colour contrasts or differences[3].

Colour assessments based on visual comparisons with sets of colour samples, known as colour order systems, can increase the range of colour designations to a few thousands [3]. The Munsell colour order system is the oldest and perhaps the most widely recognised [4], but there are at least five others [5]. There is no agreed international standard colour order system and in only a few cases have relationships been established between the various systems.

Even if agreement exists on the application of any one system, its use does not eliminate the problem of metamerism. This occurs when two colours match under one set of conditions, but fail to match under a second set of conditions [6]. Illuminant metamerism is the most important type and can occur, for example, when two metameric colours match under "daylight" but fail to match under artificial light. Observer metamerism is exhibited when two metameric colours appear to match for one person but not another. The colour vision of individuals differs to a greater or lesser extent and is also known to change with a person's age. In addition, defective colour vision in various forms is possessed by about 1 in 12 males and 1 in 200 females, so that they cannot participate in visual colour matching and have limited comprehension of colour information based on colour order systems. Colour order systems identify single colours but do not provide a way of specifying the nature or magnitude of colour differences or contrasts [7].

The limitations of visual observations may, in principle, be overcome by the instrumental evaluation of colours and colour differences according to the system of colour measurement established by the Commission International d'Eclairage [2,8,9]. This has become widely used, particularly in the last two decades, with the availability of reliable reflectance spectrophotometric instrumentation which conforms to the recommendation of the CIE for the measurement of surface colours [3,7,10].

The CIE colour system

The perceived colour of an object depends on (1) the nature of the illuminating light, (2) its modification by interaction with the object, and (3) the characteristics of the observer response. The CIE system defines these conditions as follows. (1) The relative spectral energy distributions of various illuminates, known as CIE Standard Illuminants, are specified and available as published tables [2,8]. (2) The modification of an illuminant by interaction with the object is measured with a reflectance spectrophotometer having an optical configuration which conforms to CIE recommendations [2], and provides a visible spectrum expressed as the fractions of incident light intensity reflected in the wavelength range 400 -700nm. (3) A mathematical description of human colour vision has been established for the purposes of colour measurement in terms of three colour matching functions $\bar{x}$, $\bar{y}$, and $\bar{z}$. Three are required since colour vision has been found to be trichromatic: a single perceived colour may be regarded as resulting from the effect of three separate stimuli on the visual cortex [9]. Their numerical values are available as published tables and are known collectively as CIE Standard Observer [2,8].

Colours are measured in terms of their tristimulus values X, Y, and Z by combining the illuminant, reflectance and observer data with three summations, each having the form:

$$\Sigma\ E.R.\bar{x} = X$$

At selected intervals in the wavelength range 400 - 700 nm the relative energy (E) of the chosen Standard Illuminant is multiplied by the fraction reflected (R) and the numerical value of the Standard Observer ($\bar{x}$ or $\bar{y}$ or $\bar{z}$). A wavelength interval of 10 nm, which requires 32 terms in each summation, gives adequate precision for most purposes. However, the tristimulus values of colours are difficult to relate to the experience of seeing them. In addition, in any study involving comparisions, contrasts or changes, tristimulus values do not directly enable measurement of the difference between two colours. This concern has now been overcome by using the tristimulus values to calculate the 1976 CIE L*a*b* (CIELAB) colour space values [2,7]. Colours may then be regarded as existing in a three-dimensional space in which each particular colour has a unique location defined in terms of its cartesian coordinates with respect to the axes L*, a* and b*, as shown in Fig. 1.

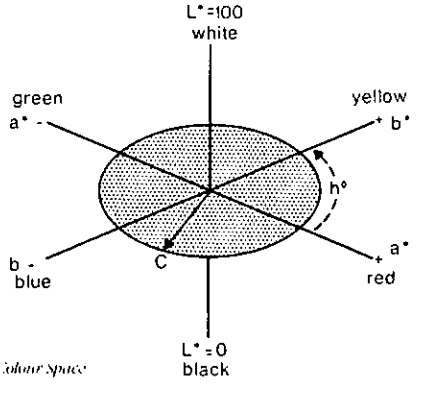

Fig. 1 CIELAB Colour Space

The measured L^* value of a colour has been recommended by the CIE as the psychometric correlate of the visually perceived colour attribute of "lightness" [2], to which the descriptive terms assigned might include the words "light", "dark", etc. In other words, L^* would measure the change along a grey scale from black to white which visually varied in a perceptually uniform manner. The L^* scale, which ranges from 0 for a theoretical black to 100 for a perfect white, corresponds to the notion of the Value attribute in the Munsell colour order system. The a^* and b^* coordinates may be conceptually related to Hering's opponent colour theory (6) which was based on the proposition that the retina of the eye contains opponent colour channels which distinguish colours according to their red versus green and yellow versus blue attributes. In CIELAB space they are more useful when converted into polar coordinates. This enables definition of a hue angle, $h^\circ = \arctan (b^*/a^*)$, which is recommended by the CIE as the psychometric correlate of the visually perceived attribute of hue (e.g., red, orange, yellow, etc.). Measured hue angles make the use of visually assigned hue terms unnecessary, although it is simple and often convenient to relate them in a general way. The general angular position of some of the main generic hues are shown in the diagram. CIE hue angle corresponds conceptually to the attribute of Hue in the Munsell colour order system but no simple relationship has been found between measured hue angle values and Munsell Hue designations. Colours for which both a^* and b^* are zero, and therefore lie on the L^* axis, are termed achromatic and would be perceived as grey, white or black. The visually perceived colour attribute of "saturation", which might be described by the use of terms pale, moderate, strong, etc., may be measured in terms of its distance away from the L^* axis in the a^*b^* plane. This is the length of the line C in the diagram. It is termed the CIE [1976] a, b chroma and is calculated using coordinate geometry as $[(a^*)^2 + (b^*)^2]^{1/2}$. It corresponds conceptually to the attribute of Chroma in the Munsell system but the measured values do not relate in any simple way to Munsell designations. Thus the use of CIELAB coordinates enables measurement of the three attributes a colour by which it is visually distinguished [4].

CIELAB space is not only more convenient than tristimulus values with respect to its conceptual relationship to the actual experience of seeing the colours but it has the important advantage of providing a means of measuring the differences between any two colours [2,7]. Their difference is simply calculated, using coordinate geometry, as the length of the line joining their coordinate positions in CIELAB space.

It has been recognised that CIELAB space is not perfect in terms of its perceptual uniformity, and colour science remains an active field of research in which the objective is to find mathematical transformations of tristimulus data to give a hypothetically perfect uniform colour space.

Colour metrology is important in many industries were the consistency and reproducibility of the colour of both raw materials and manufactured products is vital to commercial viability in a competitive environment. In a New Zealand context areas of application include raw wool specification, textile dyeing and bleaching, meat [11], dairy and other food products, pulp and paper, printing, paint, plastics, packaging, etc., etc. It has also been applied in a variety of interdisciplinary scientific studies in medicine [12], botany [13], and zoology [14], to name but a few.

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CONFERENCES

MARCH 31 - APRIL 3, 1992

THE CRYSTAL BALL CONFERENCE — an insight to your energy futures. For policy and financial analysts, business consultants, advertising agents, PR consultants, energy suppliers, energy consumers, consulting engineers and all those related to the energy market.

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N.S.W. SOUTHERN HIGHLANDS CONFERENCE ON HETEROCYCLIC CHEMISTRY

1992, August 30 - September 1

Following two very successful meetings, the third New South Wales Southern Highlands Conference will be held at Milton Park, Bowral, N.S.W., on 30 August - 1 September, 1992. While the general theme of the Conference is heterocyclic chemistry, lecture topics will include natural products and all aspects of synthetic and organometallic chemistry, pharmacology, stereochemistry and commercial developments. For further information contact Professor David St C Black, School of Chemistry, University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033, phone 61-2-697-4657.

PACIFIC RIM BIO-BASED COMPOSITES SYMPOSIUM

7-13 November 1992
Rotorua, New Zealand
Topics for symposium will include:
The Resource
Present industry - opportunities and limitations
Property-enhanced composites
New applications
Recycled composites
Wood/Non-wood composites
Fibre-fibre bonding
Forming technology
Chemical modification of wood

There will be a special one-day meeting on chemical modification of wood. The future directions of wood-based composites will be explored, as it will be for composites made from other lignocellulosics as straw, jute, flax, bagasse and bamboo.

Papers and posters are solicited on the indicated topic sessions. Abstracts (about 100 words) are due no later than 29 February 1992.

For more information, please contact:
Dr David Plackett,
Forest Research Institute,
Private Bag 3020,
Rotorua, New Zealand.

LETTER TO THE EDITOR

Dear Sir,

Roger Keen's analysis of the influence of temperature on the volume of the oceans (*Chemistry in New Zealand*, 55: 71, 1991) is completely wide of the mark with regard to the effects of global warming on oceanic sea level. The predictions of temperature increases in the range 1-5°C are based mainly on global atmospheric circulation models and concern increases in the temperature of the *atmosphere*, not the ocean. The immediate and obvious effect of such a temperature increase is to cause part of the polar ice reservoirs to melt.

At the present time, these reservoirs account for about 2.2% of the earth's water, compared with 97.2% in the ocean (the remaining 0.6% is mainly ground water). This amount of ice, spread over the surface area of the ocean, is equivalent to a water depth of about 90 metres. Thus it is not hard to see how an increase in sea level of 1-2 metres can be achieved by the melting of only a small fraction of the ice sheets.

In fact, the analysis is not quite as simple as this because of secondary effects. Firstly, an increase in sea level causes some compression of the earth's crust. Secondly, some of the polar ice is already under water and thus contributes already to the present-day oceanic sea level. Against this must be set possible catastrophic scenarios. For example, if the Ross ice shelf were to melt sufficiently to detach from the Antarctic continent, then some of the enormous Western Antarctic ice sheet would most likely just slide into the ocean regardless of whether it melted or not.

In spite of these factors, the principal control on sea level remains the quantity of ice that is held in the polar reservoirs. We know quite a lot about how this control was exercised during past climate changes through studies of the oxygen-18 isotopic content of both ice cores and benthic foraminifera in marine sediments.

Because water containing O-18 has a lower vapour pressure than water containing O-16, there is a measurable difference in the isotopic content of polar ice and the ocean that is directly related to the amount of water stored in polar ice. These O-18 studies imply that during the last glacial maximum 15,000 years ago the sea level was 70-130 metres *lower* than it is today (and the ice reservoirs proportionately larger), a finding that is supported by a host of other geological evidence.

Thus it is nonsense for Roger Keen to suggest that an *increase* in air temperature will cause *more* ice to form at the poles.

Climate-driven temperature changes in the ocean are much smaller than in the atmosphere because of the slow circulation rate of the ocean and its large heat capacity. Most of the ocean below a few hundred metres depth is below 2°C in temperature and exchanges only slowly with warmer surface waters in contact with the atmosphere. The time scale for this exchange is about 1000 years. Most deep ocean-atmosphere interaction occurs at high latitudes where the main effect is *cooling* of seawater. Most paleochemical evidence suggests that during the last glacial maximum the ocean was no more than a degree or so colder than it is today.

Finally, it is neither obvious nor correct that "deep water at the bottom of the sea would be at 4°C, since at 4°C, water has its greatest density". The density of seawater in the deep ocean is controlled mainly by its salt content, not its temperature. Temperature is the main factor only near the surface.

Dr Keith A. Hunter, Senior Lecturer,
Marine & Analytical Chemistry

EVIDENCE MOUNTS AGAINST PRECIPITATE GREENHOUSE ACTION

Over the past two months I have listened to, and participated in a tremendous amount of debate on the greenhouse effect and climate warming.

It was the subject of the feature day at the Fourth New Zealand Coal Conference, when a variety of views were aired on the possible extent of current and future climate warming and the strategies that could be used to counter it.

Shortly after the Conference, Rob Storey, the new Minister for the Environment, held an industry briefing on the Government's response to climate change, at which he reaffirmed the government's commitment to a target of reducing carbon dioxide emissions by 20% by the year 2000.

In November, I attended an IEA/OECD conference in Sydney called "Coal, The Environment and Development: Technologists To Reduce Greenhouse Gas Emissions" which discussed, among other topics, the increased energy use in developing countries in relation to the greenhouse effect.

At the New Zealand conference, keynote speaker Fred Singer regretted that the executive summary of the IPCC implied a much greater degree of certainty existed about climate warming than was evidenced by the scientific papers of the full report. He enumerated the many uncertainties that still exist in the scientific understanding of climate change and warned against precipitate action to counter effects which have not yet been scientifically proven. This position was further supported at the Sydney conference by John Zillman, the Director of the Commonwealth Bureau of Meteorology, who revealed yet another uncertainty. Some scientists have calculated that CFCs do not increase the greenhouse effect overall, as previously thought, because they destroy another greenhouse gas, ozone, in the upper atmosphere. If this is true, predictions of temperature rises would have to be significantly revised downwards. Hardly a scientific consensus on the subject!

It was remarked in Sydney that the IPCC report on response strategies had been written without waiting for the scientific assessments. Agreeing that there was a lack of consensus amongst scientists, Brian O'Brien, former Director of Western Australia's Environmental Protection Agency, identified eleven flaws in the scientific arguments used to justify a target of 20% reduction of carbon dioxide emissions.

Perhaps the most significant of the many important issues raised at the Sydney conference was the high priority that developing nations put on increased electrification, which they see as the key to their industrialisation and economic development. These countries currently account for only 15% of the world's energy use, but their populations are projected to double in fifty years and their use of electricity in ten. This will inevitably lead to a significant increase in fossil fuel use (especially coal) for electricity generation.

A number of more efficient electricity generation technologies, with very much reduced greenhouse gas emissions, were discussed at both conferences. Their efficiencies will be increased even further if they are integrated with district heating schemes of adjacent industrial processing plants. The developing countries are open to reducing emissions by adopting the latest technologies, especially with technological and financial aid from developed countries. They are not, however, prepared to take any actions which will compromise their economic development.

The New Zealand Government's briefing on their response to climate change was notable for the well orchestrated and uncompromising stand taken by environmental groups, also for the silence of the oil industry, which is responsible for half the New Zealand carbon dioxide emissions. The Minister did emphasise that government policy will not include actions which will damage our competitive advantage. Any actions should be cost-effective, make sense whether or not climate change occurs, and have a net benefit for New Zealand, he said.

He maintained an open mind about switching to a net, rather than a gross, CO_2 emissions reduction target, which would allow New Zealand credit for the carbon dioxide absorbed by new forestry plantings. Speaking at the New Zealand conference dinner, Wink Sutton of Tasman Forestry made a very convincing case for forestry planting on a large scale as the most effective way for New Zealand to reduce any carbon dioxide debt and meet the Government's criteria for response strategies.

In the end, New Zealand's biggest contribution to reducing global climate change will not depend so much on any local action as on the help it can provide to developing nations to adopt efficient energy technologies. To provide this help requires a strong economy. Stringent adherence to ill-conceived greenhouse targets will not achieve this objective.

Rob Whitney, Director,
Coal Research Association of N.Z. Inc.

(With permission from the December Coal Research Newsletter.)

PATENT OFFICE ADOPTS NEW BIOTECH POLICY

The Patent Office has put into effect some policy changes concerning the treatment of patent applications covering biotech subject matter. Last year, the New Zealand Patent Office set up a biotechnology review committee of senior Patent Office Examiners to review its policy in this area. It has recently published its conclusions.

The Review Committee considered a number of issues, including how to charactise micro-organisms, which are the subject of patent applications, and whether patent protection should be available for industrially useful micro-organisms or "biological compounds" that have been isolated from nature.

A microbiological invention may involve using a new strain of micro-organism, to produce a new compound, or to produce a known compound to a higher yield or purity. If the new micro-organism has resulted from genetic engineering, it will be patentable in New Zealand. However, problems arise if, as in many cases, the micro-organism exists in nature and has been isolated, for example, by screening soil samples. This is because the New Zealand Patent Office takes the view that the micro-organism is not new, and isolation requires ordinary skill and patience rather than inventive ingenuity.

Patenting Naturally Occurring Micro-Organisms, Protein Fragments and DNA Sequences

Patent claims to pure strains or cultures of newly isolated naturally occurring micro-organisms are, in general, allowed in the USA. The US view is that the objective of the patent system is to encourage and reward research and development. And isolating a micro-organism from nature and finding a commercial use for it can be just as difficult and meritorious as producing a new micro-organism, so patent protection should be available to encourage and reward such work.

As a result of the Review Committee's deliberation, the Patent Office has recently issued two policy directives to its Examiners.

In one of the directives, Patent Office Examiners have been instructed that patents may now be granted for naturally occuring micro-organisms and "biological compounds" provided that the patent claims are directed to the micro-organism or biological compound in a state other than that in which it is found in nature. For example, patents may now be granted for micro-organisms which have been isolated from nature, provided the patent claims are directed to the micro-organism in a stated degree of purity, or contain the wording "except when found in nature." The directive also states that claims to compounds containing protein fragments and DNA sequences will be allowed, again provided the patent claims are worded to exclude those in their naturally occurring form. Claims for processes for isolating or purifying materials from natural environments and the products of such processes remain allowable.

The Patent Office has also clarified the status of patent claims directed to metabolites of micro-organisms. The directive states that "claims to these metabolites have been allowed in the past and are still considered allowable, provided they are novel. For example, new antibiotics from previously unknown micro-organisms are analogous to any other new compound, and unlimited product claims to them are allowable".

Protein Fragments & DNA Sequences that do not Occur in Nature

The other Patent Office directive to Examiners concerns protein fragments and DNA sequences that do *not* occur in nature. This directive states that such DNA sequences and protein fragments that are defined by a sequence of amino acids, or by their functionality when compared with an aspect of the functionality of the "parent protein" may be claimed - provided that certain other standard criteria are met.

The Patent Office has held a number of patent applications in abeyance awaiting this review, and these are now being processed. These important changes bring New Zealand Patent Office practice more into line with the major industrialised countries in what is now no longer such new technology.

Characterising Micro-Organisms

A patent applicant must submit a written patent specification, fully describing and defining the invention. However, if the invention relates to a micro-organism, it is practically impossible to unambiguously define that in a written description. And even if a complete written description could be prepared, there is no guarantee that the written description will be sufficient to enable others to reproduce the micro-organism or the method of using it when the patent has expired. It is also important for other manufacturers to know whether the strain they wish to use is the patented strain.

The Review Committee has considered this problem. It has released a discussion paper, but has not yet published any conclusions. The approach which has been developed internationally to meet this problem is to require applicants to deposit of a sample of their strains into a recognised culture collection. Many countries have signed a treaty concerning the depositing of micro-organisms for patent applications. This is known as the Budapest Treaty. Under the Budapest Treaty, a single deposit at an International Depository Authority is recognised by all member countries for the purposes of patent applications filed in those countries. This means that individual deposits in each country are not required. New Zealand is not a party to the Budapest Treaty, but separate from the Patent Office's biotechnology review. The Ministry of Commerce is conducting a comprehensive overhaul of the New Zealand patent legislation and it is expected that New Zealand will join the Budapest Treaty. It is understood that the Patent Office is awaiting moves in this direction. That is likely to occur when a bill, which can be expected to substantially rewrite New Zealand patent law, is introduced into Parliament - hopefully in 1992.

Second Medical Use Inventions

The Assistant Commissioner of Patents recently made an unpopular decision concerning the patentability of the second medical use of a known compound, in a patent application filed by the Massachusetts Institute of Technology.

A researcher may find that a known chemical compound is useful in the treatmentof disease. If the compound is known, and has not been newly synthesised, it cannot be patented. However, if the pharmaceutical activity of the compound is unknown, a patent can probably be obtained for a pharmaceutical composition of the compound and a carrier. The carrier itself need not be new, just the combination. Protecting the composition in this way in effect affords protection for the first medical use of the known compound.

It is not uncommon for researchers to discover that a known pharmaceutical compound is also useful for treatment of a second disease i.e. that the compound has a second medical use. Once again, the compound cannot be patented as it is not new. In this case, it is difficult to obtain patent protection, at least in New Zealand. Such second medical use inventions can result from as much research as first medical use inventions. The European Patent Office allows a form of patent claim which gives a measure of protection for these so called second medical use inventions. This new form of patent claim takes the form of a claim for a method of manufacturing a medicament for treating a certain condition. It originated in Switzerland, and so has become known as the Swiss claim. This form of claim has subsequently been allowed in the UK.

In the MIT's application, the Assistant Commissioner of Patents had to make a decision on whether this form of claim would be allowed in New Zealand, as a solution to the problem of protecting second medical use inventions. As a result, second medical use inventions remain, in most cases, unprotectable in New Zealand.

COMPANY NEWS

SOLE NZ AGENT FOR JT BAKER PRODUCTS

JT Baker have appointed Labsupply Pierce (NZ) Ltd as their sole New Zealand dealer.

Inclusive with this dealership, Labsupply Pierce are able to offer a range of JT Baker products. Included in this range are solvents for HPLC, Trace Organic Residue analysis, environmental monitoring, trace element analysis, Ultra-Trace Organic Residue analysis, DNA/protein analysis, in addition to the Bakerbond range of solid phase extraction columns. JT Baker International has been in the business of making chemicals, and associated products, for well over 80 years. With future developments in mind, JT Baker represents a desire to move ahead of the times and strengthen their commitment to customer satisfaction. Instrumental in this commitment to customer satisfaction is the ongoing innovation in product design and quality. An example of JT Baker's dedication to product quality is shown in their development of Statistical Process Control (SPC) and Statistical Quality Control (SQC), which ensure a reproducible "built-in" quality to the product line. With this sort of company attitude it comes as no surprise that JT Baker "Baker Analysed" Reagents have been rated Number #1 in quality by Mar%Stat, USA for 13 consecutive years.

Labsupply Pierce are pleased to be associated with JT Baker International and hence are able to pass these benefits over to you through their exclusive dealership.

FOR FURTHER INFORMATION:

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NEW AGENCIES FOR RADIOMETER PACIFIC

Radiometer Pacific are proud to announce their appointment as Sole New Zealand Sales and Agents for RETSCH GMBH and SYMPATEC, both of Germany.

RETSCH have, for over 75 years, specialised in sample preparation and analysing technology. They offer a wide range of laboratory mills, grinders, crushers, sieves, shakers, sample dividers etc.

SYMPATEC of Germany are manufacturers of Laser Diffraction Particle Size Analysers, for measurement of particles from 0.1μm to 2625μm in dry powders, suspensions, sprays or emulsions, for use as Laboratory Analyzers or for ONLINE Systems in Production Analysis.

FOR FURTHER INFORMATION:

Radiometer Pacific Ltd
PO Box 12-416 Penrose, Auckland
Phone: 0-9-573 1110
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A NEW GENERATION OF PIPETTES FROM EPPENDORF

HIGH ACCURACY AND AUTOCLAVEABLE

EPPENDORF have just released the VARIPETTE 4810 series. The extended range of six Varipette models can pipette liquid volumes from 0.5ul to 2,500ul. There is one single control button for setting the volume, pipetting the sample and ejecting the tip. When the desired volume has been selected, it is locked in place preventing accidental changes. The digital volume readout is always visible during pipetting. Colour coding of the control button matches the colour code of the appropriate pipette tips. (White, yellow, blue or red).

These new pipettes from Eppendorf are comfortable in the hand, with a ribbed pipette body for a secure hold. All pipettes have slim nose cones which fit into most vessels. The 0.5ul pipettes can also use the GELoader tip designed for electrophoresis and DNA work in cuvettes, gel apparatus and 0.5ml tubes. The pipettes have been manufactured from high- quality plastic materials, stainless steel and ceramics to ensure their durability. The 4810 is largely resistant against chemicals. The entire Varipette is autoclaveable at 121 degree C (20 mins.)

In developing the new 4810 series, Eppendorf have incorporated their fine craftmanship and technical expertise to produce an accurate, precise instrument to meet the demands of the nineties.

Also available by Eppendorf is a new rotating pipette stand for up to six pipettes and a wall-mountable pipette holder, which holds three pipettes. This saves valuable bench space and is an ideal solution for hoods or lab benches with shelves.

NEW FROM WATSON VICTOR

KJELDAHL DIGESTER

Buchi have recently announced the introduction of their new Kjeldahl Digestion System. The new Digestion Unit B-426/435 along with the programmable Control Unit is the perfect partner to the now well know Buchi Distillation Unit, the B-323.

B-426/435 Kjeldahl Digestion Unit

The new digestors are designed to hold twelve samples, (B- 435) and six samples (B-426), to match the capacity of your sample throughout.

An important innovation with the new unit is the combination of digestion vessel holder, aspiration module and rack. This has several advantages. Firstly, it is possible to work outside a fume cupboard without the risk of gas or fume leaks. Secondly, the new compact design allows easy and efficient operation while occupying a minimum of bench space.

The new heating method heats the digestion vessels uniformly from the side, ensuring even boiling characteristics. Boiling chips are only required when evaporating larger volumes of water (>10ml). Temperature regulation is continuous up to a maximum of 650°C, which can be reached in only 5 minutes. This swift heating time means minimal digestion time. As an example, 1g of organic- biological material would be fully digested in 30-45 minutes.

In addition, Buchi make it easy to co-ordinate an entire Kjeldahl system since the digestion vessel is standard for all Buchi digestion and distillation units.

B-436 Control Unit

Remote control of the digestion process via the new Buchi control unit, B-436 allows complete command of the workings of one or two digestion units as well as the B-412 Aspiration and Scrubber unit.

The control unit can be used to program the heating profile in the digestion block. The programming is carried out by entering time and power steps. These parameters are stored as program data and, while they are never lost, they can be altered by PC. Operation of the unit is via the serial interface and the preselected paramaters are shown on an LCD.

FOR FURTHER INFORMATION:

Watson Victor Limited
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THE WORLD'S FRIENDLIEST THERMOMETER

It's clean, green and harmless. Keeping today's environmental problems in mind, ZEAL have added a new type of thermometer to their range, which is no fuss and easy to use. As shown recently on the television programme "Beyond 2000" the harmless green filling is fast to react, accurate and easy to read.

As with other general purpose ZEAL thermometers, it has an anti-roll cap to stop you from losing it over the side of your bench. It is 305mm long, with a temperature range of 10 to 100degC and is graduated in 1degC lots. The reinforced stirring tip allows you to stir liquid in your beaker with less chance of breakage. But if it does break, you've no harmful mercury to collect up, and the glass can be safely recycled along with your other glass waste.

FOR FURTHER INFORMATION:

Labsupply Pierce (NZ) Ltd
PO Box 34-234 Birkenhead, Auckland
Phone: Auckland 0-9-443 5867
Christchurch 0-3-358 7410

SEVEN NEW ORION METERS

The new range of Orion pH, temperature, mV and concentration meters is now available from Watson Victor Ltd. There are seven new meters to choose from, each cleverly designed, with a particular set of user requirements in mind. All models feature a ready indicator light, tactile audible keypads, user prompting and locked in display reading of results until you're ready for the next reading.

For field measurements there are 3 portable meters. An affordable, portable pH/temperature meter, the 230A is ideal for performing routine field pH measurements.

A step up, the Model 250A is also designed for field operation and features accurate two-step auto calibration and automatic temperature compensation.

The Model 290A is the ultimate portable meter for pH and ISE measurements.

And for pH analysis in the laboratory, there are four sleek new benchtop meters from Orion. The 420A is a microprocessor - controlled meter that gives you the basics for fast, accurate pH measurement.

The Model 520A offers all these features with the option of a combination pH electrode.

For concentration and pH measurement, with the option of a data collection, the 720A is the model to choose.

The Orion Model 920A is the top-of-the-line meter, which offers all the features you need for advanced analysis: automatic recognition of anion or cation ISE's, temperature- corrected concentration measurement, direct reading in any concentration units and data review any time.

AN AA WITH COLOUR DISPLAY

ICI INSTRUMENTS PRESENT

The popular GBC904 and 905 atomic absorption spectrophotometers are now available with a VGA colour video display. The double beam 904 and single beam 905 have an inbuilt computer and high density disk drive and incorporate automatic setting of wavelength, bandwidth and gas flows. A new software system utilises easy-to-read menus and a comprehensive colour graphics package. The system stores the graphics traces for all samples, and allows them to be recalled and displayed at any time.

FOR FURTHER INFORMATION:

Natalie Potter
ICI Instruments
5 Lake Drive
Dingley
Phone: 0-3-552 4555
Facsimile: 0-3-551 7440

NEW PH METER FROM RADIOMETER

Radiometer has developed completely new pH meters for the MeterLab range.

The main features of the new design are extreme user- friendliness and the highest standards in terms of accuracy and precision, combined with a new and modern style.

The PHM92 Lab pH Meter (two decimal places) is suitable for general laboratory use.

It is easy to operate as a result of the autoread and autofocal functions.

PHM92 is only fitted with five function keys, but built-in facilities ensure that accurate results are obtained by automatic one or two-point calibrations and by manual or automatic result reading.

A stability indicator on the two-line display plays a leading part in all the measurement operations.

One or two-point calibrations are made straightfoward and easy with the autocal facility, and the electrode signal - once stable - is loaded into memory.

The calibration values are retained in the memory, even if the PHM92 is switched off.

Built-in interface facilities make it possible to connect a computer/printer and an analog recorder to PHM92.

FOR FURTHER INFORMATION:

Radiometer Pacific Ltd
PO Box 12-416 Penrose, Auckland
Phone: 0-9-573 1110
Facsimile: 0-9-573 1106

NEW FROM WILTONS

NEW BROOKFIELD VISCOMETER

Brookfield Engineering Laboratories has released the DV-III, a programmable Rheometer ideal for both R & D and quality control applications.

The DV-III features a four-line by 24 character alphanumeric display and keypad, allowing the user to input, store and recall up to 10 multi-speed test programmes. Measurement of shear rates, shear stress values, CPS and % scale (Brookfield units) are all available while the built-in microprocessor simplifies testing and data analysis.

When more advanced analysis is required, Brookfield Rheocalc sofware controls the DV-III from any IBM PC-AT compatible computer. The software allows control of the Brookfield thermosel controller for integrated viscosity / temperature tests between 50 - 300°C. Rheocalc features include collection of up to 200 data points, automatic calculation of Casson Yield Value, Brookfield "Thix indes" and Power Law Index. On-screen and printed plots of % scale versus spindle speed, CPC vs spindle speed, CPS vs shear rate, shear rate vs shear stress and CPS vs Temperature.

DV-III Viscometers are available in LV, RV, HA and HB ranges with standard spindles or cone/plate system, and are compatible with all Brookfield accessories.

NEW VERSATILE SPECIFIC GRAVITY DETERMINATION KIT

At this year's ACHEMA Exhibition, Sartorius presented a new development: the YDKO1 Specific Gravity Determination Kit, which can be used with many of the laboratory balances made by Goettingen-based manufacturer. Among the compatible balances are the new RC, AC and LC model series, as well as the A series in the field-proven MP8 microprocessor version. The user has the choice of employing this kit with balances of different readability, with 3, 4 or 5 decimal places, all it takes is a simple exchange of the adaptor for the weighing system.

To make the user's work easier, Sartorious engineers designed the kit for high mechanical stability. In this way, the kit can be readily installed on the balance. Easily accessible sample holders of generous size are provided with the kit for measurements in air and in a medium causing buoyancy. The special design of the perforations on the holders prevents air bubbles from adhering to them. The standardized glass plummet, also available in a metrologically verified version, allows simple determination of the density of liquids.

Detailed information is given in the brochure entitled "New 'Uplift' for Your Laboratory Routine"

NEW LOW-COST, LOW MAINTENANCE CO_2 MONITOR

Detects Hazardous Gas Concentrations

A new, low-cost, low-maintenance gas monitor has been introduced by ADC Limited to warn personnel of potentially hazardous carbon dioxide (CO_2) levels.

Designed for wall-mounting, the ADC 2000 continuously monitors CO_2 levels in enclosed areas where concentrations may exceed safe levels. Installation is recommended in breweries, fermentation rooms, transport containers and any poorly ventilated working areas.

An auto-zero calibration facility minimises maintenance requirements. At regular intervals, the unit automatically corrects for ambient variations in temperature, pressure and humidity.

The unit monitors CO_2 from 0-2.0% or 0-0.3% and displays gas concentration on an easy-to-read LED panel. An alarm function activates when either of two preset concentrations are exceeded. For inaccessible installations, a remote slave unit is available with duplicate alarm functions.

FOR FURTHER INFORMATION:

Wilton Instruments
PO Box 31-044, Lower Hutt
Phone: 0-4-697 099
Facsimile: 0-4-697 240

DRY SURFACE RADIOACTIVE MEASUREMENT OF HARVESTER FILTERS

Dry Surface Counting (DSC) is the direct measurement of ionising radiation on a membrane or a filter surface with position sensitive detectors. DSC is rapidly becoming an alternative to liquid scintillation counting (LSC) as a means of evaluating filters produced by various cell harvesters, including Inotech, Skatron, Cambridge and others.

Alphatech Systems has a range of DSC instruments from Berthold and Inotech. The MSC 2000 makes use of the position-sensitive proportional counter which enables it to measure up to 24 samples simultaneously. The instrument has a capacity of up to 2000 samples. The MSC 2000 is capable of evaluating, for example, 192 samples (two sets of 96 filters) in 3-5 minutes. In this short time, all the samples are counted and results presented both graphically on a VGA screen and in a hard copy report.

DSC instruments do not use scintillation fluid or vials, bags or similar consumables. They can also be used for scanning of radioactivity – labelled DNA, RNA, protein blots, TLC plates, paper chromatograms, tissue sections etc. All common isotopes including ^{3}H, ^{32}P, ^{125}I, ^{61}CR, ^{35}S, ^{14}C, can be counted as well as other beta, gamma and alpha emitters.

FOR FURTHER INFORMATION:

Alphatech Systems
Telephone: 0-9-770 392
or 0-4-389 3905

NEW FROM ALPHATECH

WATERS SYSTEM FOR CARBOHYDRATE ANALYSIS BY PULSED AMPEROMETRIC DETECTION (PAD)

A packaged solution for high-sensitivity and gradient carbohydrate HPLC analysis.

The non-metallic 625 Pumping System with fully automated seal wash is designed to resist the corrosive effects of aggressive solvents. It is a state-of-the-art low dispersion gradient HPLC solvent delivery system. The specially engineered pulseless post-column reagent addition system ensures low dispersion mixing to maintain the high resolution of your separations.

The Model 464 Pulsed Electrochemical Detector is 20 to 40 times more sensitive than refractive index for measuring small amounts of carbohydrates.

For the Bioresearcher the WATERS Carbohydrate Analysis PAD System is superb for profiling the released oligosaaccharides from glycoproteins and for measuring monosaccharides after hydrolysis of the oligosaccharides.

For the food researcher the Carbohydrate Analysis System is excellent for measuring low level (2-10ng) carbohydrates in food samples.

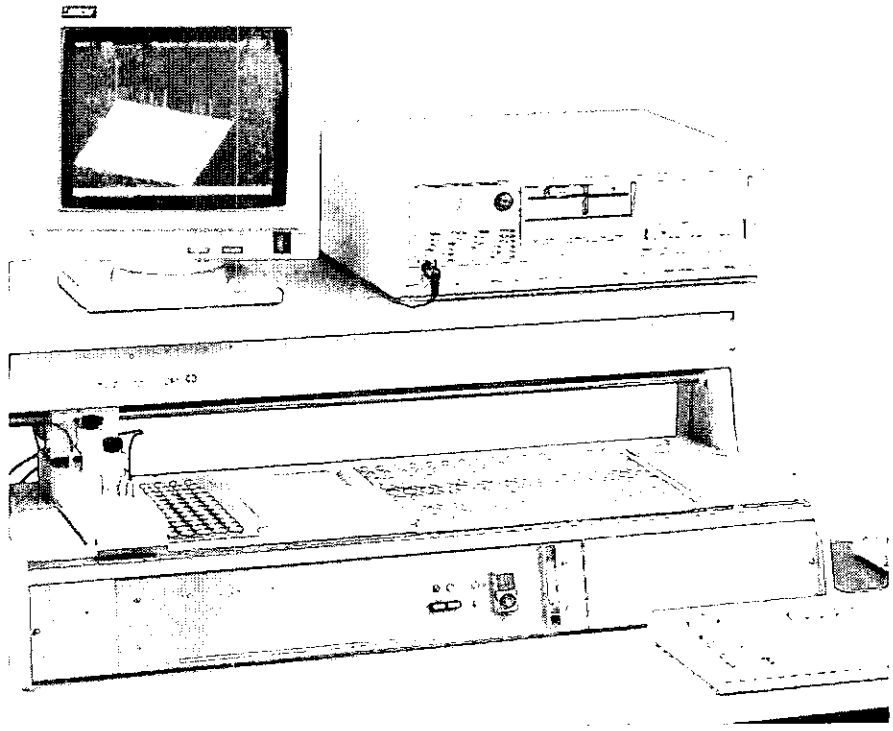
WATERS INTRODUCE A NOVA PAK C18 CARTRIDGE COLUMN

Cartridge Columns have gained acceptance with many customers as the quality of packings have improved. However, most would agree that the number of returned cartridges and batch to batch reproducibility have caused problems for them.

WATERS Nova Pak C18 is one of the best, most reproducible, high performance packings in the world. Nova Pak has low surface activity and is exhaustively end-capped making it ideal for the analysis of basic components. Nova Pak is a dense 4 μm spherical packing which leads to a rugged robust cartridge with a long lifetime.

WATERS columns are manufactured in a U.S.F.D.A. Certified Medical Device Manufacturing facility using current good manufacturing practices giving us the best possible batch to batch reproducibility so your separation works every time. Our Cartridge columns are packed on a new automated column packer and individually tested on an automated column testing machine to ensure that packing is as reproducible as synthesis of the Nova Pak C18 packing material.

Re-usable end fittings on a disposable cartridge ensures that this high efficiency, high quality material is available to improve your analysis at a price that is easy on your consumable budget.



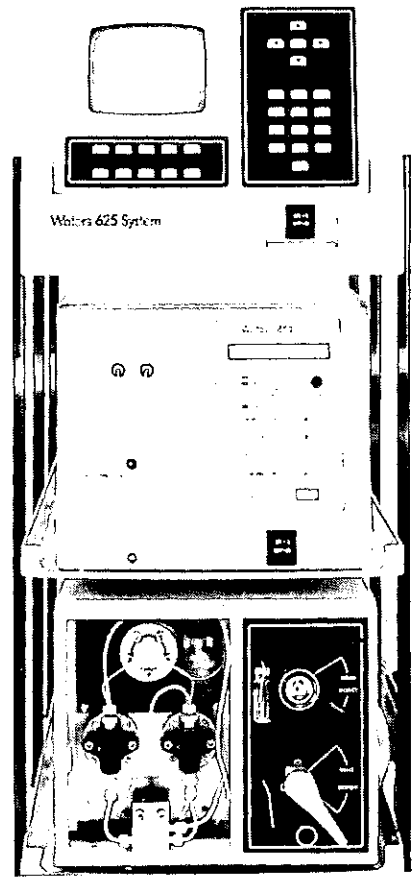
NEW ION EXCHANGER FOR PROTEIN PURIFICATION

Waters Protein-Pak™ HR chromatography packings feature a macroporous (1000 Å) polymeric base material with a high capacity for biomolecular binding and a rigid structure for high linear velocities.

The hydrophilic nature of the resin ensures minimal non-specific adsorption. Protein-Pak HR ion exchangers are compatible with aqueous acids, bases and buffers in the pH range of 2 to 12. Protein-Pak HR are available with DEAE, a weak anion exchanger, or SP, a strong cation exchanger.

Three different particle sizes (8 μm, 15 μm and 40 μm) offer the range of resolutions necessary for analysis and purification of biomolecules. Unlike other ion exchangers for protein purification, Protein-Pak HR packings are synthesized with the same chemistry on all particle sizes. The buffer system used on the 8 μm packing can be used on the 15 μm and 40 μm packing yielding identical separation selectivity. Predictability of results makes scale up of isolation procedures easy and convenient.

The Q and CM chemistries will be available shortly with 8 μm, 15 μm and 40 μm packing material.



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