



DIAKYNE PTY LTD  
(ABN 70 099 168 402)

## TECHNOLOGY & PRODUCT INFORMATION



## TraceSmart Technology

A smarter way to analyze trace elements in fluids

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## The Diakyne Technology

Diakyne has developed an innovative technology (the “Technology”), centred on Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). It is a breakthrough technology platform using ‘real-time’ mass spectrometry for very accurate essential element and heavy metal contaminant analysis. Its primary applications are in health and for testing metallic micro-concentrations in oils for machinery wear and tear.

With the further development planned following recapitalisation of the Company, it will allow rapid, automated, cost effective quantitative analysis of metallic micro-concentrations in fluids.

Presently, the Technology allows the simultaneous analysis of up to fifty (50) elements in human blood at a cost equivalent to a large number of the single element analyses currently being performed. The test is performed on a single drop of blood (chemically unmodified 50-100 microlitre volume) adsorbed onto an inert collection matrix (the nub of Diakyne’s technology).

In essence, the Technology has three parts:

- i) a standardised, proprietary collection device (the “collection matrix”);
- ii) a processing methodology; and
- iii) secret knowledge.

The parts i) and ii) are subject to a PCT filing (priority date April 2003), whilst iii) is intellectual property and methods developed and guarded by Diakyne.

The first target market for the Technology’s application is the quantitative analysis of essential elements, vital to well being, and heavy metal toxins in people’s blood. The Technology may be easily applied to the same analysis of other body fluids such as sweat and urine. The vital importance of this application is discussed at length later in this document.

The Technology could be used for mass screening of populations, particularly for the early diagnosis of trace element associated disease. Diakyne believes it will facilitate proactive remedial intervention to target and correct essential element imbalances and/or toxic heavy metal excesses.

The Technology’s other main use is for rapid and simple testing of wear and tear in machines. This may simply be done by analysis of a single drop of machine lubricant for micro-metallic concentrations.

This application has a perceived broad market in the mining industry, for automotive and haulage fleets, and the military, shipping and aircraft transport industries where a large reduction in machine downtime for periodic performance testing would be of great economic value.

Although not a focus of the Company at this point, the Technology may also be applied to analyse bloodstock, livestock and pets to identify essential element



aberrations and heavy metal toxicity in body fluids. In particular, for example, it could enable identification and rejection of heavy metal-contaminated slaughter animals designed for human consumption.

### Business Model

Since the Company's foundation in 2002, the Diakyne Board has focussed on the Technology's potential for the human healthcare market. This is because:

- a) Diakyne's development of innovative technology centred on LA-ICP-MS allows very accurate, cheap and rapid testing of essential elements in fluids at concentrations of less than 20 parts per billion. Testing by an independent laboratory, using Diakyne's Technology, has **reproduced 'in house' results for some 38 essential elements at better than 98% accuracy in metal concentrations of less than 20 parts per billion;**
- b) Scientific research and popular publication of the consequences of essential element aberrations, has focussed public awareness on their long term impacts on human health; and
- c) The burgeoning and multi-billion dollar market for self-prescribed health and nutritional supplements in the developed world conscious of wellbeing and dissatisfied with proposition of chronic malaise compromising lifestyle, especially with encroaching old age.

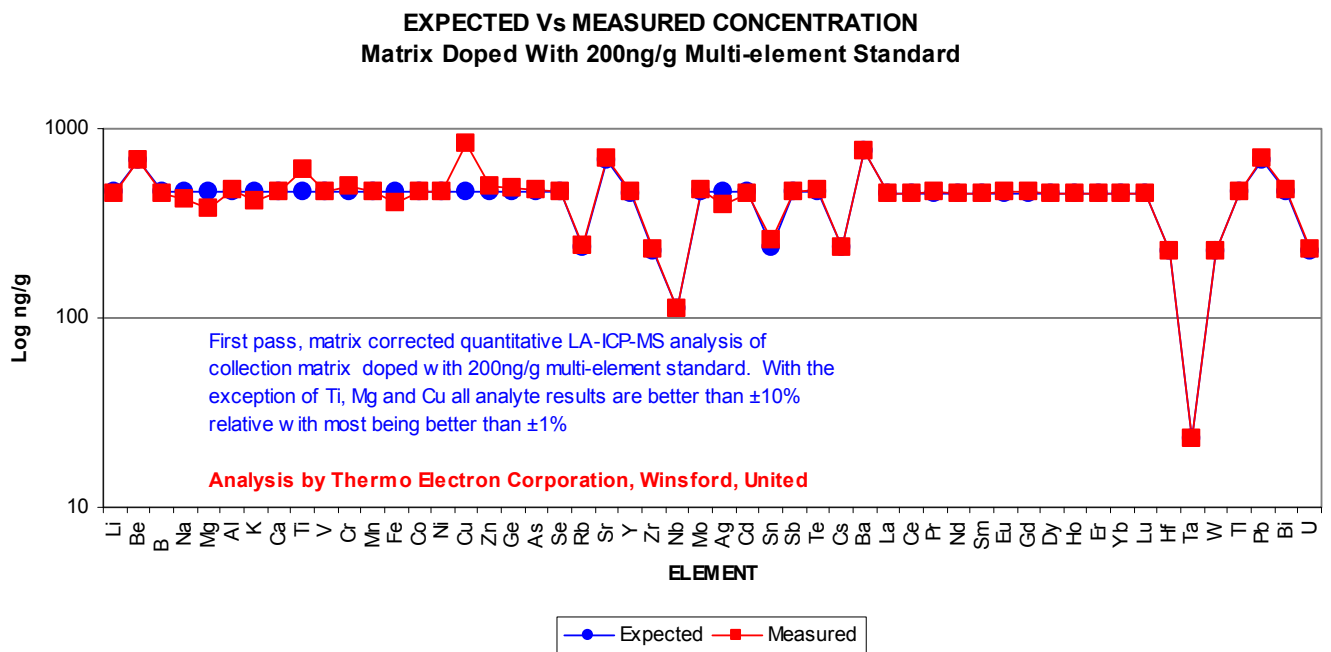
After two years Diakyne remains focussed on this potential as its primary market application. However, with sufficient resources the Company intends to widen its focus to accelerate the Technology's application in other areas, particularly the testing of machines for wear and tear.

To achieve its commercial aims, the Board has resolved to showcase its Technology then expand the market by competitive tension. With the development of a fully automated system to exploit the Technology being an estimated 18 months from initiation, the Company has still to achieve its showcase through a less efficient, but effective, manual input system. Automation of sample processing will more than double sample throughput.



# Results

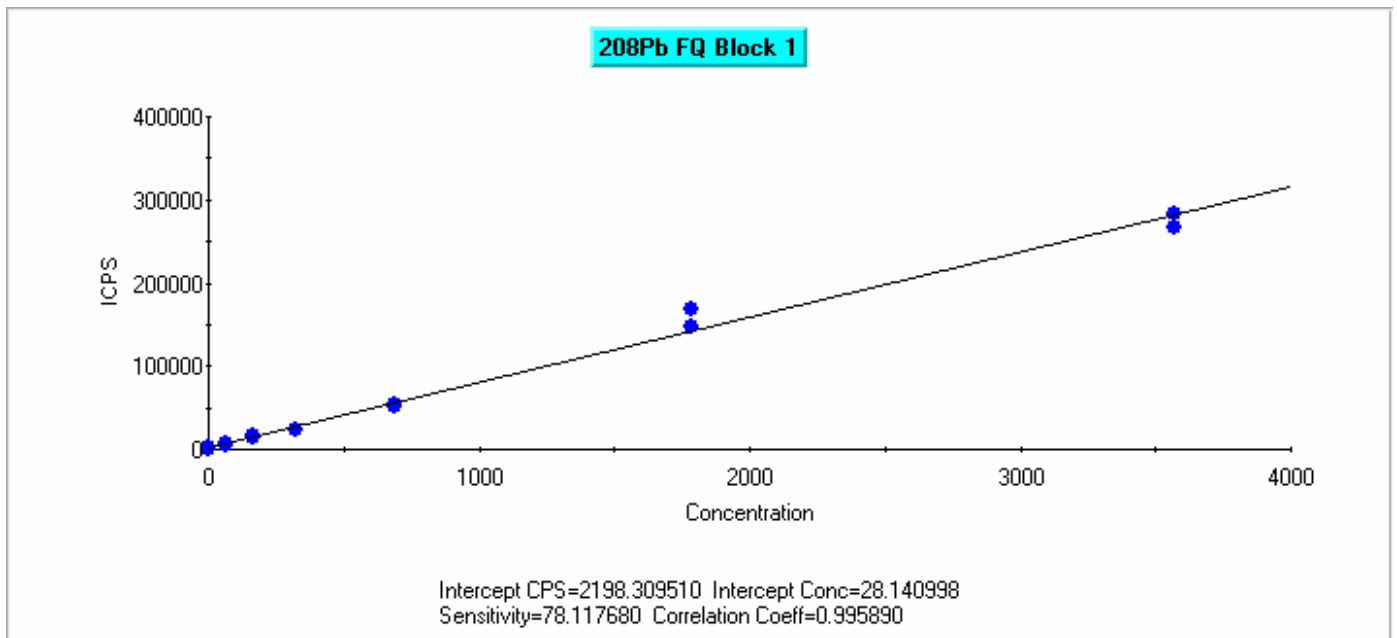
For 52 elements measured, most give measured values within  $\pm 1\%$  of expected values



# Results

## TraceSmart successfully tested

Calibration over a range of concentrations produces linear regressions with correlation coefficients  $>0.99$  for most analytes

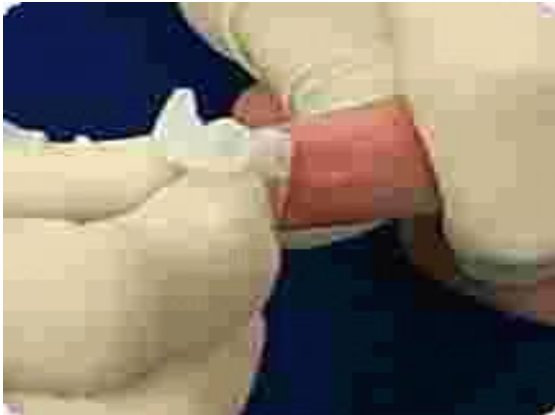


# Comparative Advantages

	TraceSmart - Diakyne	Existing Technologies
No. of analytes	>50 per sample; simultaneous	Usually <4 per sample
Test Time	<90 seconds per sample	Variable, often several minutes
Sample Volume	30 to 50 $\mu$ L (Single drop)	5 to 10 mL
Preservation	Not required	Required
Sampling	Finger prick, self-acquired or by medical professional	Vein extraction, by Pathology or medical professional
Sampling Device	Retractable, single use lancet	Hypodermic syringe
Comfort	Essentially non-invasive	Invasive, often traumatic
Sampling safety	High, minimal risk	Potential for needle stick injury
Cost	\$A100 for up to 50 elements	\$A10 to >\$A50 per element
Transportation	Absorbed dried sample	Blood filled vials
Sample Prep	None	Significant solution preparation

## Protocol for Collecting Fingerstick Blood Samples in Micro-Vials

Caution: Treat all human blood as if it could transmit infectious diseases, e.g. Hepatitis, HIV etc. (wear fresh "powder-free" gloves for each patient)



Description of Analyses and QA/QC Procedures from the National Center for Environmental Health.

# Preferred OEM Hardware



**X-Series ICP-MS system** Thermo  
Electron Corporation

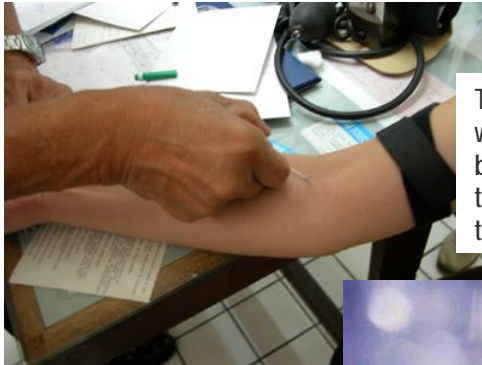


**UP 266nm Macro\* Ultraviolet  
Laser System**  
New Wave Research

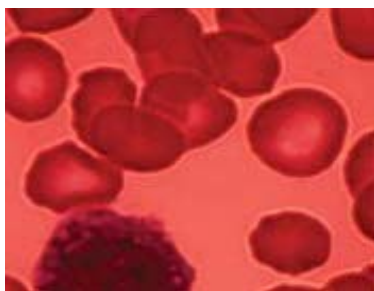
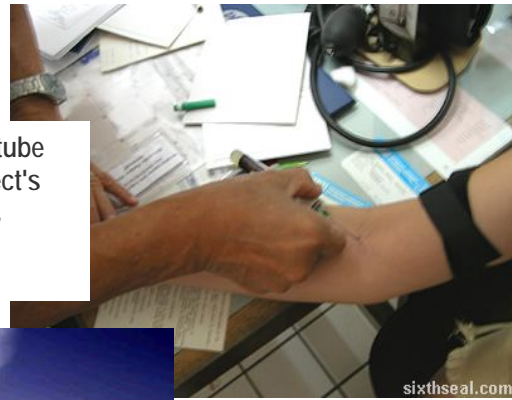


## Not Required for Diakyne Blood Tests

The doctor registers a vein and starts to draw blood.



This is the test tube where the subject's blood sample is transferred for testing.



## The Process

The diagram on the following page explains the Diakyne process.

A pinprick of blood is obtained from the patient and deposited on the Company's unique absorption matrix that is encapsulated within a bar-coded collection device. The collection device is sealed and sent to the analytical facility for analysis. The analytical process produces an aerosol of the sample that is introduced into an argon plasma, operating at approximately 8,000°C.



Trace elements in the aerosol are ionized in the argon plasma. The ionized sample enters the Mass Spectrometer separating the ions into 'channels' according to their mass to charge ratio. Each trace element is identified by its ion's unique mass to charge ratio by an ion detector. A computer report of the trace element composition is then generated and interpreted by the relevant health service provider.

## Regulatory Approval

No regulatory approval is required to operate this technology in the Australian market. However, the Company will seek regulatory approval from foreign authorities (e.g., CE mark in Europe, US FDA) for the use of its technology as a diagnostic for trace element imbalances.

The clinical trial protocol used in non-US markets will be US FDA approved protocol at a pre-submission hearing. The US approval process is expected to be via the 510k route protocol, taking less than 12 months. Upon submission of clinical data to the FDA, the regulator is obliged to respond within 90 days but it is not obliged to grant a market approval.

In Australia, the Company may employ a pathologist with an Approved Pathologist Provider Number to attract the Medicare rebate. This would facilitate adoption of the Technology by the domestic general practitioner market.

In the US, 510k approval should give it Market Approval status for medical rebate there. At this stage, the Company has not researched the medical rebate systems in other major potential markets.

## First Sales

The Company expects to achieve revenues from commercial sales of its blood test product within 12 months of recapitalisation. This is dependent upon achieving sufficient funding and the ready availability of hardware. It is also assumed a contract manufacturer can be engaged to mass-produce the standard sample collection device. The Company has already located an appropriate laboratory at the University of Queensland.

Diakyne's first product for commercial use will be a test for quantitative measurement of trace (essential and toxic) elements in human blood for determination of element aberrations by clinicians.

The broad test will allow the simultaneous analysis of up to fifty elements. The test can be done at the equivalent price to a large number of single element analyses currently performed, but will be at a modest premium (\$A100 per test). All tests will be from a single drop of blood placed on the Company's unique absorbent sample collection device.

Sample collection is essentially non-invasive and non-traumatic, eliminating the potential for needle stick injuries, serum storage, transport and waste disposal biohazard issues presently faced by healthcare workers.

## Technology in Detail

Diakyne has a breakthrough technology platform using 'real-time' mass spectrometry for very accurate, rapid, simple and cheap analysis of micro-metallic concentrations in fluids. In its primary application, the Diakyne Technology allows for the analysis of essential elements and heavy metal contamination in body fluids for health and medical diagnostics.

The Company is also developing wider applications for its Technology, particularly in the fields of machine wear and tear and also in materials testing (including pharmaceuticals) for purity.

Diakyne's innovative technology is centred on Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). With further development it will allow rapid, automated, cost effective mass screening of general populations.

Diakyne believes its technology will facilitate proactive remedial intervention to target and correct essential trace element imbalances and/or toxic heavy metal excesses. In livestock, for instance, it could enable an economic method for identification and rejection of heavy metal-contaminated slaughter animals designed for human consumption.

Presently, the Technology allows the **simultaneous analysis of up to fifty elements from a single blood drop at a cost equivalent to a large number of single element analyses currently being performed by pathology laboratories**. The analysis is performed by processing a chemically unmodified 50-100 microlitre volume of body fluid sample (single drop), absorbed onto Diakyne's unique sample collection device (an inert collection matrix, patent pending), through a mass spectrometer after vaporising the blood with a high energy laser and ionising the product aerosol in an argon plasma.

Because of the economics of the Technology, it may allow cheap, cost effective mass-screening for disease prevention using trace element discrepancies in individuals as specific disease indicators beyond current tests such as iron deficiencies. This would offer a major revenue stream similar to that for Haem (iron) tests now on the market.

In human diagnostics, the sample collection device, and collection protocol, eliminates the use of hypodermic syringes and, hence, potential for needle stick injuries. It is essentially non-invasive and non-traumatic, and does not involve the preservation, movement and storage of large volumes of blood, urine and other body fluids, or involve large biohazard disposal facilities.

Indeed, in the case of humans, samples may be self-acquired at any geographic location and dispatched to the nearest analytical facility by post or courier. Because an approximately 8,000°C argon plasma is involved in ionisation of the samples, the body fluid products are expected to be largely sterilized during analysis.

The Diakyne technology has been developed around, and successfully tested, using research facilities based on an ultraviolet laser and quadrupole inductively coupled plasma-mass spectrometer (LA-ICP-MS) with manual sample handling.

The research conducted up until the end of October 2004 indicates:

- better than 95% precision for a wide range of elements using the analytical protocols developed for this project and ICP-MS;
- sub 20ppb (parts per billion) detection limits for a wide range of elements simultaneously; and
- accurate quantitative data, using matrix matched certified reference materials, for other equivalent Certified Reference Materials, may be achieved.

### *Independently Verified...*

Subsequent work done by the Company, and independently by Thermo Electron Corporation at Winsford, GB, has reconfirmed the earlier research. In fact, detection levels for the majority of essential elements at parts per billion can be measured with an **accuracy of 98% or better** from improvements recently engineered in the sample collection device.

### *No current technology .....*

There is no current technology available that can conveniently be used for the collection and broad-spectrum analysis of the trace metal content of large numbers of blood and other body fluids samples.

Presently, available testing methods are cumbersome and expensive. For example, single element tests may cost more than \$A200 but most fall in the range of \$A25-150 and, for a restricted array of say fifteen 'routinely' analysable trace elements, either essential or toxic, analytical costs may be of the order of \$A750-1,500 per sample. This clearly places the service outside the reach of the general population, particularly in underdeveloped regions where problems are often greatest. Furthermore, these costs preclude general health insurance underwriting.

Present test methodologies require relatively large volumes of fluid samples (for example, 5-10 ml of blood). They are commonly trace element specific. i.e., simultaneous measurement of other trace elements potentially present is not possible. Because of this, other relevant trace metals are either overlooked or require further fluid samples and additional tests for their determination.

In the case of blood, this involves invasive, often traumatic extraction, particularly for young children and the elderly, using hypodermic syringes. The derivative body fluid products require stabilisation and preservation and, having regard for transmissible disease such as HIV, appropriate biohazard handling and disposal.

### **Pricing in the Australian Market**

The Company's business model is predicated on the use of the Technology by medium to high-income earning patients of alternative medical practitioners who would be prepared to pay at least **\$100 for each full trace element blood test**. For comparative purposes only, we provide below, in Scheduled Fees table, the scheduled fees for various trace element tests currently available from pathology companies in Australia.

The scheduled fee, the federal government rebate subsidy, is payable at 100% for a small minority (about 5%) of patients who meet stringent eligibility criteria. For the vast majority of patients (about 65% of all patients), the government pays 85% of the scheduled fee – this percentage applies to out-patients. The

government pays 75% of the scheduled fee for in-patients who account for approximately 30% of all patients. Patients are not generally required to pay any money at all as nearly all tests are bulk billed.

**Table Scheduled Fees**

<b>Item #</b>	<b>Description</b>	<b>Fee</b>
66566	Potassium, ionised calcium	\$33.25
66584	Calcium	\$9.55
66593	Ferritin	\$17.80
66596	Iron studies	\$32.10
66665	Lead quantitation	\$30.20
66667	Serum Zinc re intravenous alimentation	\$30.20
66669	Copper, Manganese, Selenium & Zinc I	\$30.20
66670	Copper, Manganese, Selenium & Zinc II	\$51.75
66671	Aluminium	\$36.40
66672	Arsenic, beryllium, cadmium, chromium, gold, mercury, Nickel, strontium I	\$30.20
66673	Arsenic, beryllium, cadmium, chromium, gold, mercury, Nickel, strontium II	\$51.75

Source: Health Insurance Commission web site

[www.hic.gov.au/statistics/dyn\\_mbs/forms/mbs\\_tab4.shtml](http://www.hic.gov.au/statistics/dyn_mbs/forms/mbs_tab4.shtml)



## Diakyne Blood Tests determines Mineral levels so that nutrition and vitamin regimes can be rationalised with accuracy

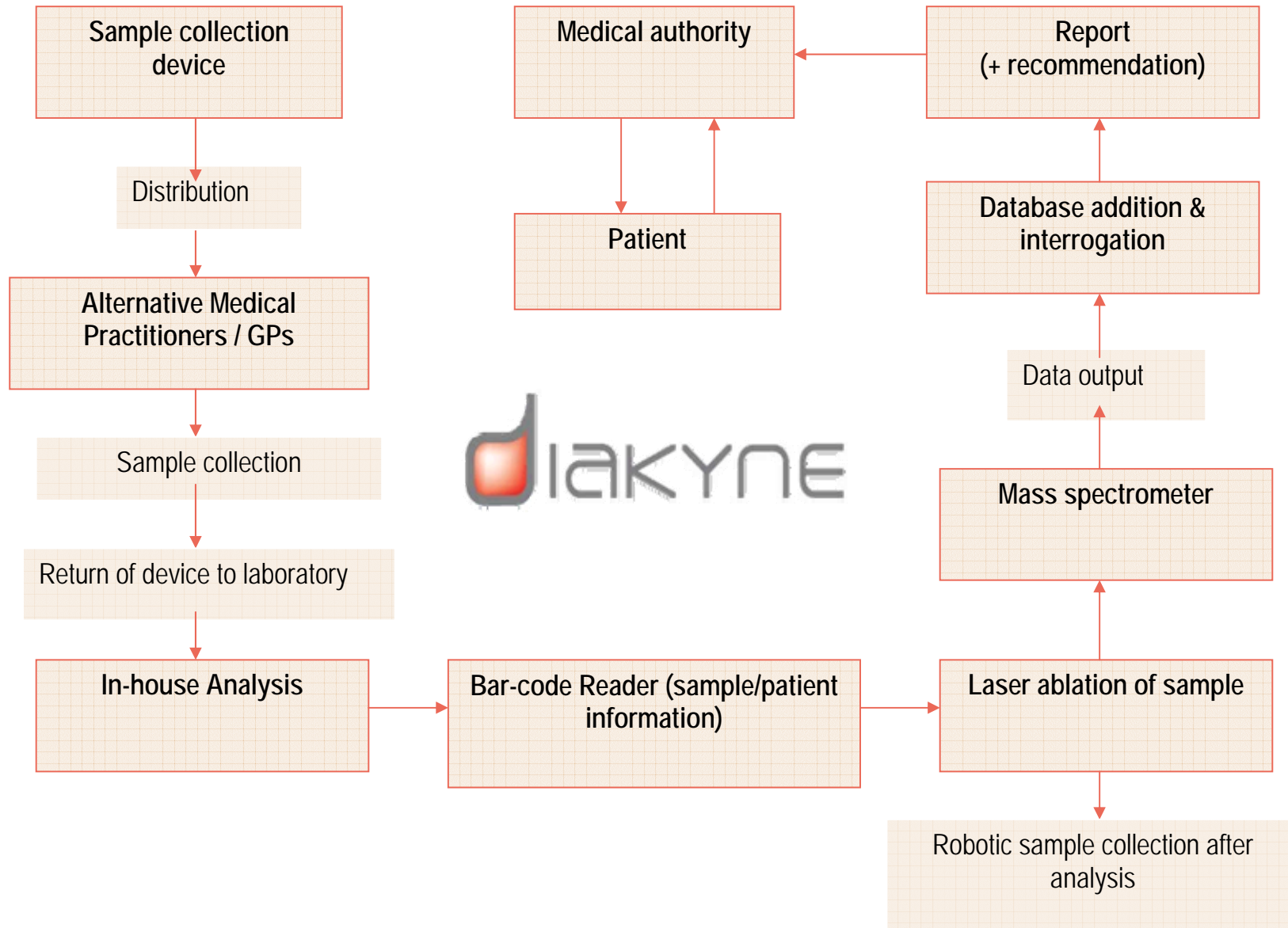
<b>Mineral Chart</b>		
<b>All The Vitamins and Minerals Our Bodies Need</b>		
Nutrient	Suggested	Function
Boron	Toxic at 1 gram - no RDA	Bone health
Calcium	DRI 1,000 - 1,300 mg to 2.5 grams	Health of bones, teeth, muscles, regular heartbeat, and nerve function
Chromium	Tolerable intake 200 - 400 mcg	Metabolizes insulin
Copper	Tolerable intake up to 2 mg	Aids in iron absorption. synthesizes hemoglobin, produces energy
Flouride	DRI 3.1 mg - 10 mg	Health of bones and teeth
Iodine	RDA 150 mcg	Necessary fro thyroid hormone
Iron	RDA 15 mg	Formation of red blood cells.
Magnesium	RDA 320 mg - 350 mg	Aids muscle function, supports teeth and cardiovascular system
Manganese	Upper level intake to 2 mg	Formation of bones and collagen, metabolizes carbohydrates, synthesizes fatty acids and protein
Molybdenum	Upper level intake 10-25 mcg, upper levels to 50 mcg	Metabolizes iron, works with enzymes
Phosphorous	RDA 800 mg DRI 700 mg	Health of bones and teeth. Works with enzymes
Potassium	Upper level intake 200 mg	Balance of fluids. Supports function of nerves, metabolizes protien and carbohydrates. Aids in muscle contraction
Selenium	RDA 55 mcg	Antioxidant, prevents damage to cells
Vanadium	Upper level intake to mcg	Metabolizes cholesterol and blood sugar. Possibly works with hormones
Zinc	RDA 12 mg	Utilized in conjunction with enzymes. Contributes to health of immune and reproductive systems

## Vitamin Chart

### All The Vitamins and Minerals Our Bodies Need

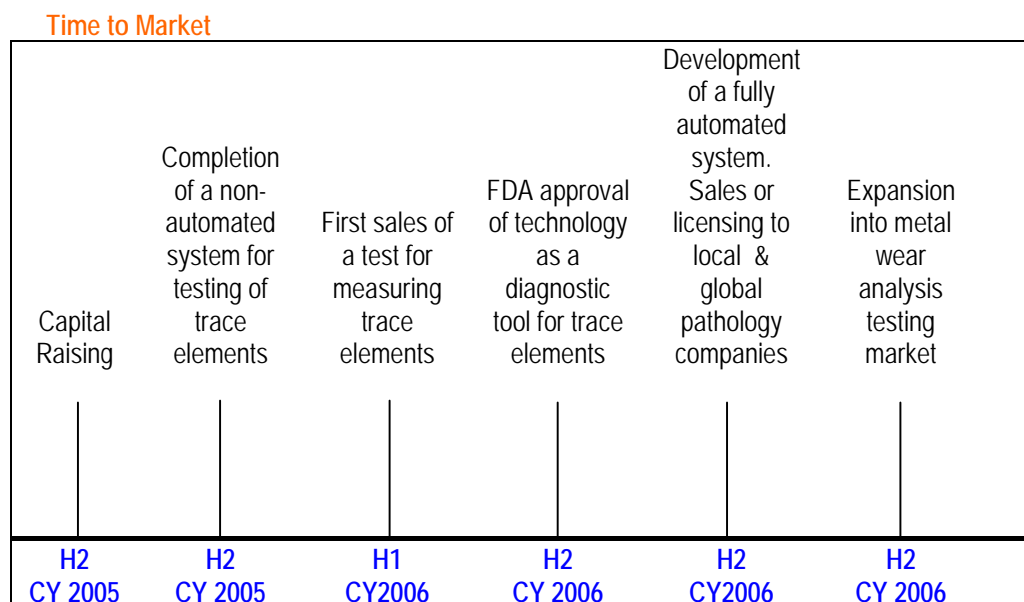
Nutrient	Suggested	Function	Toxicity/Issues
Vitamin A (retinol)	RDA 1,000 mcg or 5,000 IU	Maintains and promotes growth of tissue, bones, and teeth. Important for mucous membranes and vision	Intake of over 2,500 IU daily may cause birth defects
Vitamin A (beta carotene)	No RDA set	Antioxidant, protects against cancer	Non toxic
Vitamin B1 (thiamin)	RDA 1.1 mg	Supports growth, muscles, and nerve function. Necessary for utilization of carbohydrates	Some toxicity concerns
Vitamin B2 (riboflavin)	RDA 1.3 mg	Needed to metabolize amino and fatty acids. Formation of red blood cells and antibodies	Some toxicity concerns
Vitamin B6 (pyridoxine)	RDA 1.6 mg	Forms antibodies, synthesizes hormones. Metabolizes protein	Over 500 mg daily can damage nervous system
Vitamin B12	RDA 2 mcg	Metabolizes protein, carbohydrates and fats. Maintains nervous system and formulates blood cells	Gastrointestinal illness impairs absorption
Biotin	No RDA DRI 30 mcg	Metabolizes fats, carbohydrates, and protein.	Non toxic
Vitamin C	RDA 60 mg	Vital to strong immune system. Promotes healing of wounds. Antioxidant, maintains healthy blood vessels. Iron utilization	Gastrointestinal illness impairs absorption
Choline	No RDA DRI 10 - 100 mg	Builds neurotransmitters - part of brain function	Non toxic
Vitamin D	RDA 5 mcg, upper levels to 50 mcg	Sustains health of bones, proper utilization of calcium, created by exposure to sun.	Non toxic
Vitamin E (D-alpha tocopherol)	RDA 5 mcg	Antioxidant, maintains cell membranes. Protects lungs, liver, skin and breast tissue	Some toxicity concerns
Folic Acid	RDA 180 mcg DRI 400 mcg	Forms red blood cells and necessary for cell division. Used in digestion, metabolizes protein.	Non toxic
Vitamin K	RDA 65 mcg	Utilized for blood clotting and calcium binding.	Gastrointestinal illness impairs absorption
Niacin	RDA 15 mg DRI 14 mg	Aids in healthy cells, nervous system, skin, and digestive function.	Non toxic
Pantothenic Acid	DRI 5 mg	Helps synthesize fatty acids and cholesterol.	Non toxic





## Time to Market

The timetable below outlines the key milestones.



The Company expects to produce a non-automated, beta commercial system for the testing of trace element aberrations in human populations in Brisbane within 12 months of raising the necessary initial funding of about \$A1 million. This is provided the Company can take delivery of a suitable LA-ICP-MS system within two months of recapitalisation. The system analyser will be owned and operated by the Company at a laboratory at the University of Queensland.

A fully automated system is expected to be operational within a further 12 months with the raising of an additional \$A3 million and the development of an automated sample insertion device.

Revenue is expected to increase rapidly once global markets are accessed in 2008.

## Sustainable Competitive Advantage

The sustainable competitive advantage of Diakyne's Technology is evinced by:

- The developed product will enable the mass screening of a variety of blood or other body fluid samples for a wide range of essential and toxic trace elements.
- The test will require only a small volume of sample liquid (one or two drops).
- Sample collection of body fluids will not require the use of a hypodermic needle and consequently will be essentially non-invasive and considerably safer than existing methods. The sample will be collected and stored in an inert matrix without need for addition of preservatives.
- The sample can be handled and transported safely and easily.

- The samples will be automatically analysed for a wide range of elements.
- The proposed method of analysis, Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry is very sensitive and can detect and measure trace/ultra trace amounts of an element.
- The design of a fully automated analysis system, along with the interpretation software for the data, will enable high throughput screening and analysis of samples.
- Further, the Diakyne technology will offer multi-element testing at a significantly lower cost than many current single element tests, thus making the economical mass-screening of target populations possible.

## Market Entry Strategy

### A. Initial Entry

As referred to earlier, Diakyne's first product for commercial use will be a test for quantitative measurement of essential elements and metal toxins in human blood for determination of element aberrations by clinicians.

The business model the Company intends to implement is centred on showcasing the Technology within Australia as a means of attracting foreign companies to assist in the worldwide distribution of sample collection devices to alternative and general medical practitioners. The population segments targeted are those people most likely to voluntarily spend money on mineral supplementation for remedial and/or preventative purposes.

These people are likely to be the patients of alternative medical practitioners such as chiropractors, dieticians, osteopaths, herbalists, homeopaths and naturopaths. The relevant population also includes regular health club members/users, competitive sports players and ageing 'baby boomers'.

The broad test will allow the simultaneous analysis of up to fifty elements at about \$A100 a test. The test may be comprehensive (all elements in the range) or selective (a specified cluster of elements).

Regardless of the quanta, it is the same process for the same cost. A report generated for the querist would show only the test results requested.

Pricing will be competitively structured. Diakyne projects \$A100 is a commercially viable price to sell a test for a wide suite of trace elements. This is based on the price of current tests for commonly analysed individual trace elements that can cost up to \$A51.75 each (see Table 3). All tests will be from a single drop of blood placed on the absorbent sample collection device.

Reiterating, the Company will initially produce a non-automated, beta commercial system for the testing of trace element aberrations in human populations in Brisbane. The system analyser will be owned and operated by the Company at an appropriate laboratory at the University of Queensland.

A fully automated system is expected to be operational within a further 12 months with the development of an automated sample insertion device.

## **B. Detailed Marketing Report**

The Company commissioned an extensive marketing report in relation to the testing of human blood in Australia. The report identifies the relevant population segment, market size, appropriate means of disseminating the Company's message and the key people the Company needs to contact. A SWOT analysis was also prepared by the marketing firm. A copy of this Report accompanies this document.

The report provides Diakyne with great encouragement as to the potential for its product in the health care market. The unexpectedly lower level of enthusiasm for the Technology showed by chiropractors surveyed in the Report was offset by the much greater than expected interest displayed by mainstream general practitioners.

PruCon also identified key opinion leaders in the healthcare market relevant to Diakyne that the Company intends to capitalize on actively.

The Company recently commissioned Prudence Consulting to start the second stage of the Marketing Report and Public Awareness Strategy. It starts in early July and is expected to be completed in the final quarter of 2005.

As part of this exercise, Diakyne with PruCon will meet and present to the key people in the market to establish strategic relationships and promote the Technology ahead of its launch.

The Company was awarded a grant from the New South Wales Department of State and Regional Development to cover half of the costs pertaining to the fees to be charged in relation to the preparation of the above-mentioned marketing report. It is entitled to a similar award for the second stage.

## **C. Entry of the Automated System**

In the first year of commercialisation of the automated system, the local Australian market will be expanded rapidly through a territorially-based licensing model similar in concept to franchising.

Overall, a relatively good rate of market penetration is expected annually thereafter in the local market. The penetration percentages are forecast to increase from 5% in 2006 to 20% in 2009. It is envisaged all testing will initially be performed at a laboratory managed by the Company itself. Refer to Table 5 for the estimated number of eligible patient tests per year from CY 2005 to CY 2009 for Australia, the United States, Western Europe and the rest of the world.

### ***Foreign Joint Venture Arrangements***

The United States and Western European markets will be entered in 2007. The most likely avenue of penetration is through joint venture arrangements with pathology companies in those regions. Diakyne may enter into a number of Original Equipment Manufacture ("OEM") arrangements. With an OEM, the purchasing pathology company would buy the sample collection devices and then put their label on the devices. Diakyne would profit from the sale of the devices whereas the pathology companies would profit from the testing process itself.

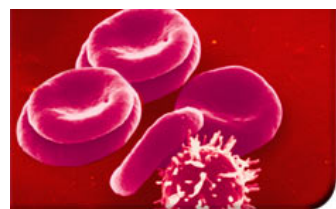
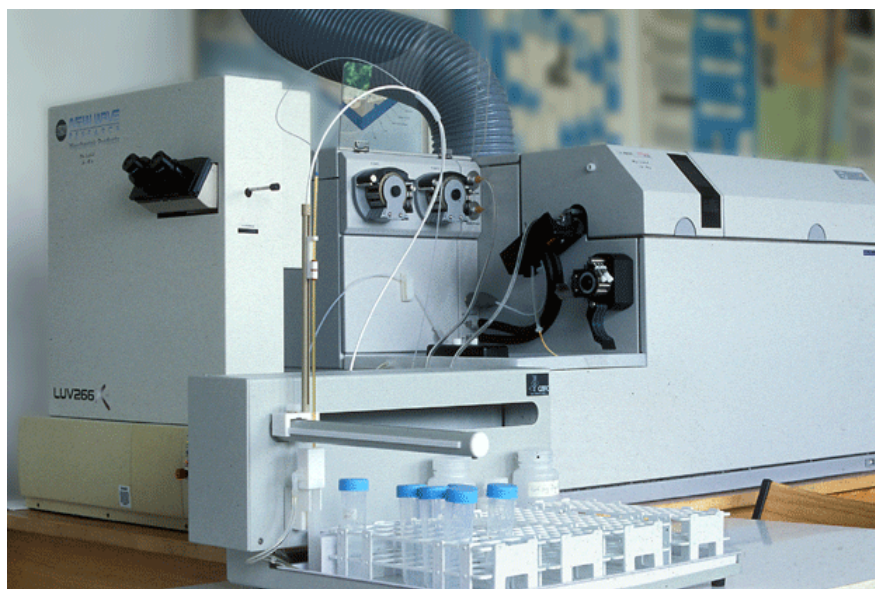
As such, the cost to Diakyne of operating in foreign jurisdictions may be minimal. Diakyne will not need to establish laboratories or employ any staff, other than marketing staff. It is estimated the Company will be able to charge the foreign pathology companies \$A10 per sample collection device for both individual and full trace element testing.

## Patent Estate

The core Diakyne Technology is covered by PCT application, proprietary knowledge and undisclosed IP and methodology.

The Company recently completed the National Phase of the International Patent Protection process. Patent claims were lodged in the following jurisdictions: Australia, New Zealand, USA, Europe, China, India, Canada, Japan, Brazil, Korea and Israel.

In 2004, the Company was awarded a grant from the New South Wales Department of State and Regional Development to cover one quarter of the costs pertaining to the National Phase of the International Patent Prosecution process.



## Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS) equipment for the analysis of solid samples

<http://www.gfz-potsdam.de/pb4/pg3/equipment/laicpms.html>

### (a) LA-ICPMS Basics

A laser beam is focused via a petrographic microscope onto the sample surface. The sample is placed within a sample cell, where the ablation takes place. The sample cell is flushed with argon. During interaction of the laser beam with the solid sample small amounts of sample (particles, clusters, free atoms, ions) are ablated and transported with the argon flow as carrier gas to the ICP for ionisation and subsequent analysis in the mass spectrometer.

Fig.1: VG Elemental UV Microprobe



### (b) Equipment

Laboratory is equipped with a VG Elemental UV Microprobe (Fig. 1) coupled to a VG Elemental PQX-S inductively coupled plasma mass spectrometer. The laser ablation unit is schematically shown in Fig. 2. Basic component is a horizontally mounted Minilite (Continuum) Nd:YAG. The fundamental wave length (1064 nm, infrared) is converted to his fourth harmonic (266 nm, UV). The laser beam is folded through 90° onto the sample surface via a petrographic microscope. The ablation target can be viewed in-situ through a CCD camera for precise location of the analysis site. Samples are mounted in a cell on a high precision X:Y:Z stage, which can be driven either manually (keypad) or automatically (software). The sample cell is flushed with argon gas, carrying the ablated material to the ICP.

Fig. 2: schematic setup of laser ablation unit

### (c) Advantages of LA-ICPMS

- Direct analysis of different types of solids
- No chemical procedures for dissolving resulting in reduced risk of contamination and sample losses
- Analysis of very small samples which cannot be separated for solution analysis
- Determination of spatial distribution of elements

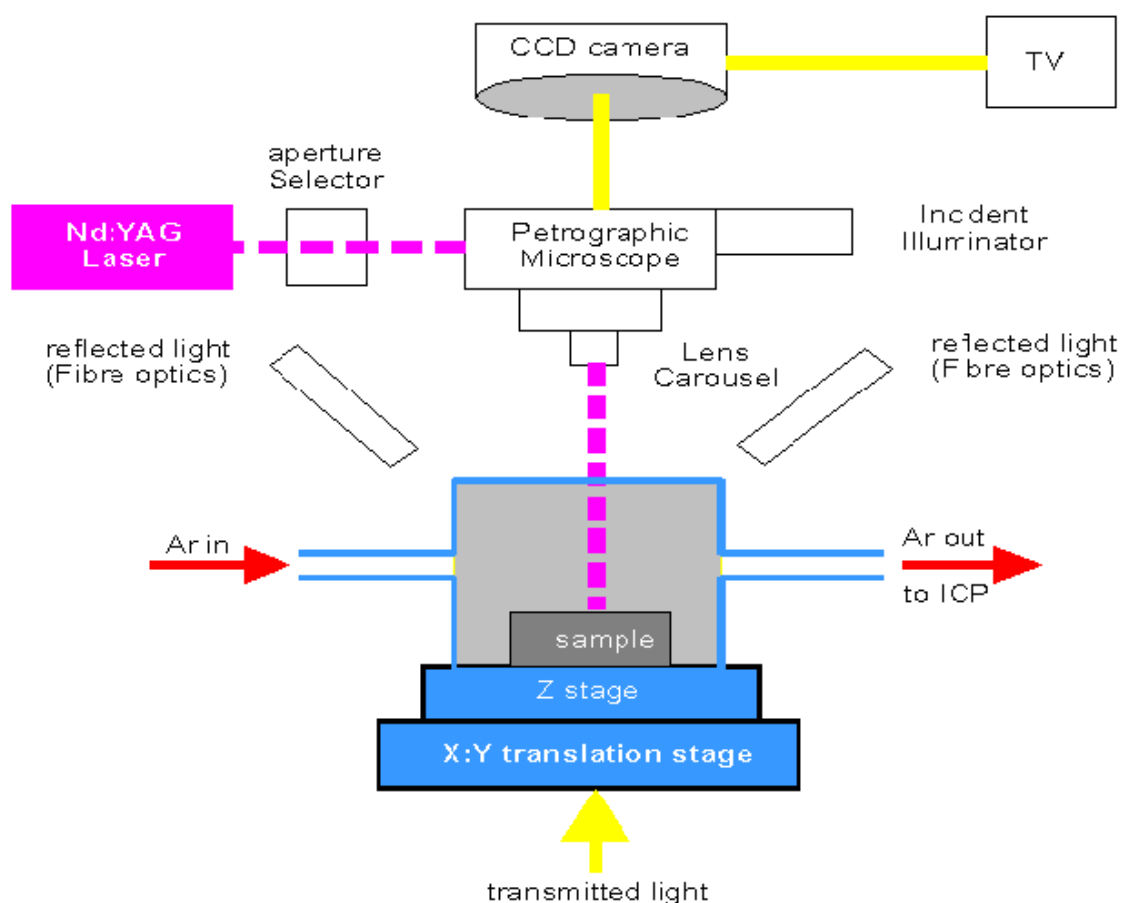
**(d) Problems**

- Contamination of sample surface during cutting processes
- Internal standard to correct for differences in the ablation rate of sample and standard (determined by different technique, stoichiometric factor, added to sample)
- Calibration

**(e) Geological applications**

Fields of application of laser ablation ICP-MS in the earth sciences are the whole variety of geological samples (rocks, minerals, glasses, fluid and solid inclusions).

- Bulk analysis of powder samples pressed powders with and without binder, pressed pellets, tetraborate fusion to a glass, sample powder embedded in epoxy.
- Bulk, local and distribution analysis of solid samples small to larger samples (depending of the dimension of the sample cell), thin and thick sections.





## Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS)

**LASER ABLATION-INDUCTIVELY COUPLED-PLASMA MASS SPECTROMETRY (LA-ICP-MS)** <http://www.nhm.ac.uk/research-curation/science-facilities/analytical-imaging/laicpms.htm>

LA-ICP-MS is a highly sensitive method to quantitatively and qualitatively analyse constituents of a sample by detecting a mass of grains, which were vaporised and dispersed when the sample was irradiated by a high-energy laser beam of shorter wavelength on its surface, and then ionised by plasma generated by high frequency power (Fig 2).

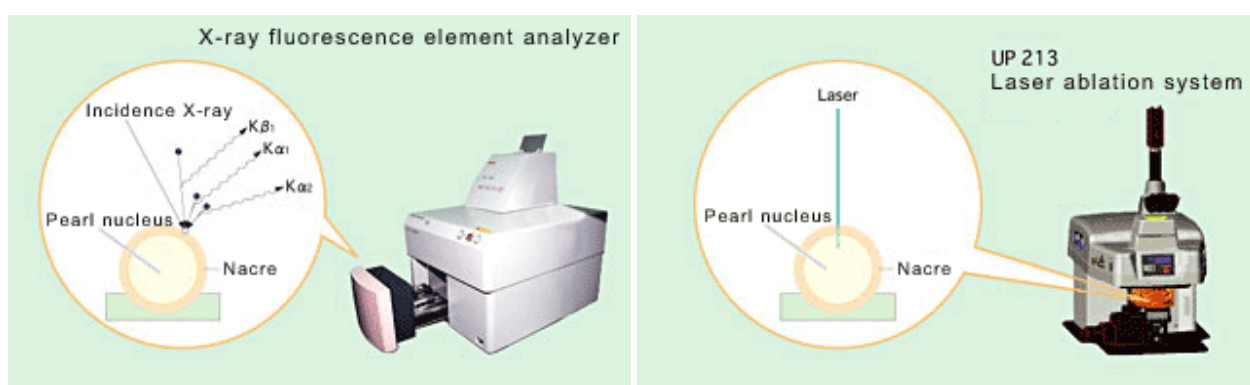


Fig.1 Schematic diagram of an X-ray fluorescence element analyzer.

Fig.2 Schematic diagram of the LA-ICP-MS analytical device.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is one of the most successful direct solid sampling techniques for major, minor and trace element analysis. However, this technique still suffers from matrix dependent ablation characteristics, which makes quantification very difficult. Furthermore, the laser sampled material alters its composition from the sample to the detector.

ICP-MS is the method of choice for fast, trace level elemental analysis, with multi-element detection limits below ppb for solutions and ppm for solids.

In addition to the analysis of samples in solution, we have a Microprobe II laser ablation system (LA-ICP-MS). Laser ablation avoids the need to dissolve samples and allows precise spatially-resolved microanalysis of solid samples.

Instrument Thermo Elemental PQ3 +S ICP-MS with New Wave UP213AI laser

Resolution 5 - 130 microns

Elemental range Li to U, see [Periodic Table](#)

Main applications Micro determinations of trace elements, REE and mineral ages in polished samples.

Sample media Uncoated polished sections and blocks, some unpolished unmounted media.





## Periodic Table showing elemental range and typical detection limits for ICP-AES

Typical detection limits

- ICP-MS: <0.005 ppm in solution
- ICP-AES: 0.005-0.1 ppm in solution
- LA-ICP-MS: 0.005-1 ppm in solution but prone to interferences, very matrix dependent, not usually for natural samples
- CHNS: (not specified in legend)

H																			He
Li	Be											B	C	N	O	F		Ne	
Na	Mg											Al	Si	P	S	Cl		Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br		Kr	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I		Xe	
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At		Rn	
Fr	Ra																		
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb				
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No				

The LA-ICP-MS system consists of a Thermo Elemental PlasmaQuad 3 quadrupole based ICP-MS with an enhanced sensitivity S-option interface, coupled to a New Wave Research Universal Platform 213nm aperture imaged, frequency quintupled laser ablation accessory. The instrument is capable of the simultaneous determination of 40 trace elements in less than two minutes. Most elements from lithium (7 amu) to uranium (238 amu) can be determined, with detection limits in the range of a few ppb for most elements.

For LA-ICP-MS analyses, samples are held in an air tight cell, flushed with helium. The laser is fired at the sample and sub-micron particles are ablated and picked up in the flow of helium. Argon gas is added to the flow just prior to its injection into an argon plasma. At temperatures as high as 10,000 K, the sample particles are readily ionised in the plasma. A mass spectrometer is used to separate the ions according to their mass to charge ratio, after which they are counted.

The instrument is used for a wide range of research projects including the determination of trace elements and REE in mineralogical samples, U-Pb age determinations for a range of minerals (e.g. zircon, monazite and titanite), fluid inclusion analysis, forensic, archaeological and fingerprinting applications, the analysis of trace elements in biologically derived solids including human teeth and bones.

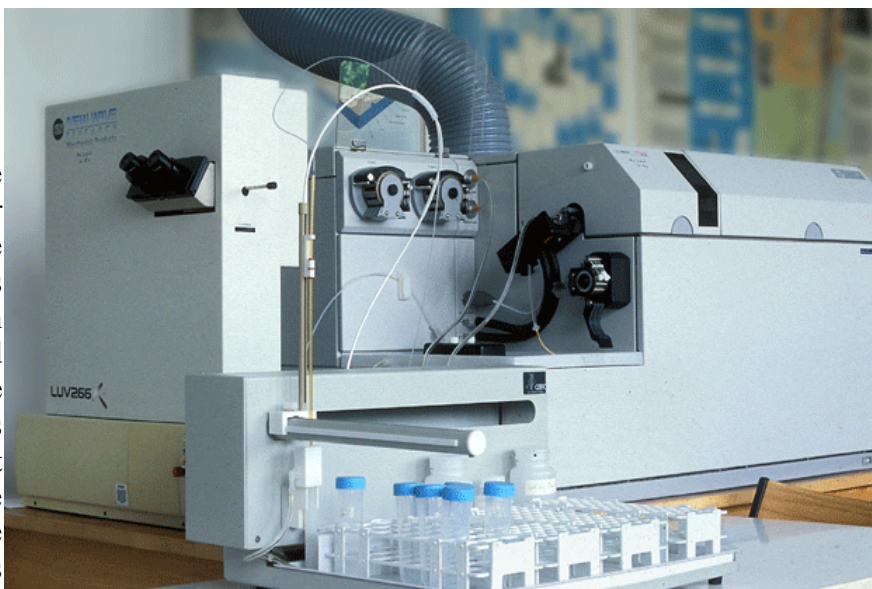
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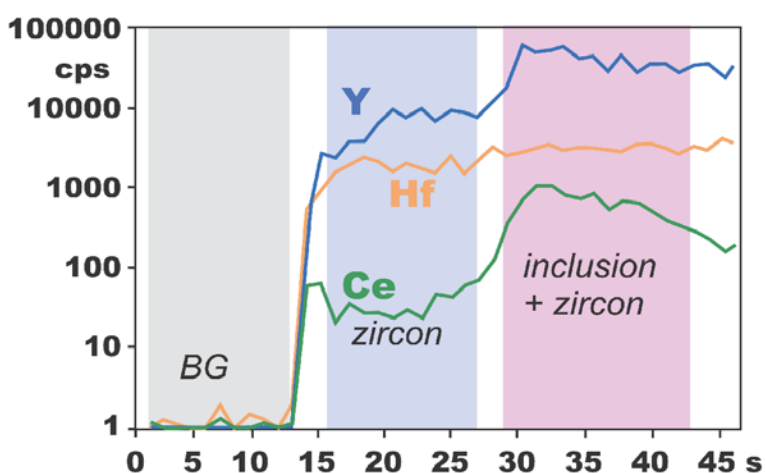
## Laser Ablation (LA-ICPMS) at the Institute of Mineralogy, University of Würzburg

<http://www.uni-wuerzburg.de/mineralogie/icpms/icpms.html>

Laser ablation is the most versatile in-situ solid sampling technique for ICP mass spectrometry. The focusing characteristics of lasers permit sampling of small areas, such that localized microanalysis and spatially resolved studies are practicable. The signal intensity is directly proportional to the amount of ablated material transported to the ICPMS. Laser-generated signals are transient but time-resolved-analysis mode allows evaluation of every single section of the signal, whatever lateral or depth profiling (Figure 1).



Quantification of the signal occurs via several reference standard material (NIST 610, NIST 612, NIST 614, DLH 5, DLH 6, DLH 7, DLH 8, DLH 20; garnet K23; zircon 91500) which are ablated with the same laser conditions as the unknown samples. The count rate obtained for a particular ion is compared with a calibration plot to give the concentration for that element in the sample. The reproducibility of the LA-ICPMS data is superior at lower levels, due to detection limits below the ppm level.



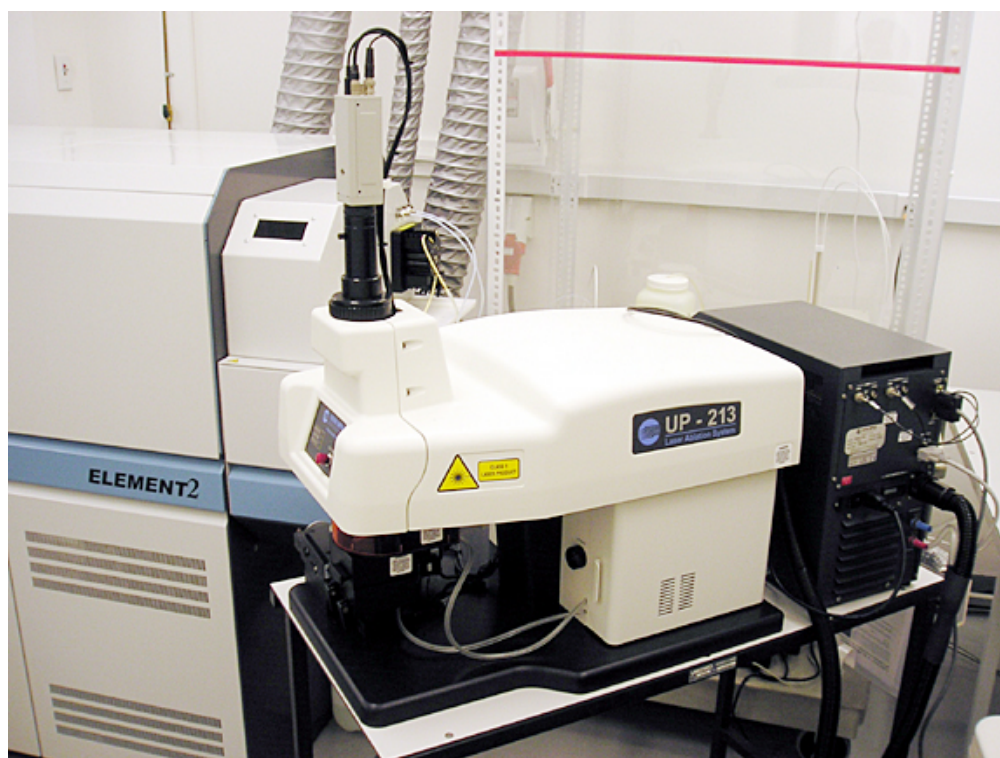
● Laser Ablation

Coupled with the ICPMS is a Merchantek New Wave UV Class 1 laser system which provides a means of rapid, direct analysis of solid samples without the need for lengthy chemical preparation and the benefit of minimal sample preparation. The UV laser contains a frequency-quadrupled 266nm Nd:YAG laser

capable of delivering an energy of 4 mJ to the sample site. A proprietary beam delivery system generates a Flat-Top beam profile which can be controlled to generate spot sizes < 30 up to 400  $\mu\text{m}$  in diameter. The laser unit is provided with a polarization microscope and a high resolution CCD camera to view the sample. Different light sources (transmitted/reflected/collateral) for sample illumination and a micron adjustable stage permit extremely precise micro-sampling. Ablation patterns can be varied (single spot, line of spots, line, raster etc.) according to the respective application.

### ● Inductively Coupled Plasma Mass Spectrometry

Sample introduction from the laser ablation unit to the ICPMS occurs via a tygon tube. A high temperature argon plasma dissociates, atomizes and ionizes the sample to produce a cloud of positively charged ions. The sample ions are extracted from the plasma and passing through the sample and skimmer cones into the mass spectrometer. The Agilent 7500i has a triple-stage vacuum system with a rotary pump for the expansion region (interface) and two turbo-molecular pumps for the intermediate and analyser stages. The ion optic lens system can be adjusted manually to provide optimum ion transmission and high signal sensitivity. Ions are focused through the quadrupole mass analyzer, where they are separated on the basis of their mass-to-charge ratio ( $m/z$ ) by varying the RF and DC voltages. These voltages are ramped very rapidly so the quadrupole can scan the whole mass range (2-260 amu) in 100 milliseconds. As a result, spectra of mass versus intensity can be obtained for all elements virtually simultaneously. Quadrupoles are limited effectively to unit mass resolution so they can't resolve polyatomic and isobaric interferences. However, of all of the elements detectable by ICPMS, only indium does not have an isotope that is free from overlap by another element. The ion signals are measured by the electron multiplier detector which operates in pulse mode for low and in analog mode for high concentrations samples.



## Chemical Analysis Through the Use of Laser Ablation Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS): A Provenance Study of Virgin Branch Anasazi Ceramics in the American Southwest

<http://www.csulb.edu/depts/geography/gdep/posters03/anasazi/>

### Laboratory Methods

- Once brought into the laboratory, the raw clay and sherds are ground into a fine powder.
- Water is added to the clay to make a small patty that is then baked in a furnace at 850 degrees Celsius for one hour to simulate the ceramic.
- The clay is then ground into a fine powder once again and it, along with the ground sherds, are placed into labeled vials.



- 0.3g of the powdered clay and sherds are then separated for further testing and, from this point forward, all conditions of the sample are recorded.
- An internal standard of 0.5 ml (40 ppm) of Indium solution is then added to the samples for quantification control, and the samples are placed in an oven at 50 degrees Celsius overnight.
- The samples are weighed and mixed in a mixer mill for 30 minutes.
- Then they are transferred into different vials, while the weight and loss of the sample are recorded.
- Binding powder is then added to the sample bringing it to a weight of 0.5 grams.
- The samples are then pressed into pellets about 13 mm in diameter and are then ready to undergo LA-ICP-MS.
- LA-ICP-MS, a relatively new technique, is capable of multi-element characterization of many materials including glass, metal, lithics, and ceramics. Once the ceramic sample is placed into a laser chamber, a laser beam is used to ablate a small area. The ablated materials are then introduced to the ICP-MS torch to be ionized. These ions are separated based on mass and charge. They are sent to a detector which then can provide compositional data for 50-60 elements.





