Identification of Improvised Explosives by Capillary Electrophoresis (CE) and Ion Chromatography (IC)

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Http://www.across.utas.edu.au

What are Inorganic IEDs?

- "Homemade" explosive devices employing strong inorganic oxidisers such as nitrate, perchlorate or chlorate
- Inorganic IEDs are favoured by terrorists due to their ease of attainment
  - chemicals are not restricted
- Bali Bombing 2002
  - Two suicide bombers and a car bomb detonated outside of Sari Club
  - It was found to contain potassium chlorate, sulfur and aluminium
  - The marker ion, chlorate, was detected using a bench-top Capillary Electrophoresis (CE)

Counter-Terrorism Programs

- Pre-blast and post-blast identification of explosives using measurement of inorganic anions and cations
- Post-blast trace detection systems for homemade explosive devices
  - Inorganic based explosives
- Pre-blast screening systems for improvised explosive devices
  - Inorganic and peroxide based explosives
- Development of dedicated explosive analysers for use by police agencies, forensic laboratories and protective services around the globe

Post-Blast Project

Post-Blast Project Aims

- To produce a series of Ion Chromatographic (IC) and Capillary Electrophoresis (CE) systems meet the following specifications:
  - Identify explosives by analysis of post-blast residues.
  - Provide more sensitive and faster analysis compared to current methodologies.
  - Suitability for miniaturisation leading to field-deployable, and ultimately, portable instruments

Homemade Explosive Devices

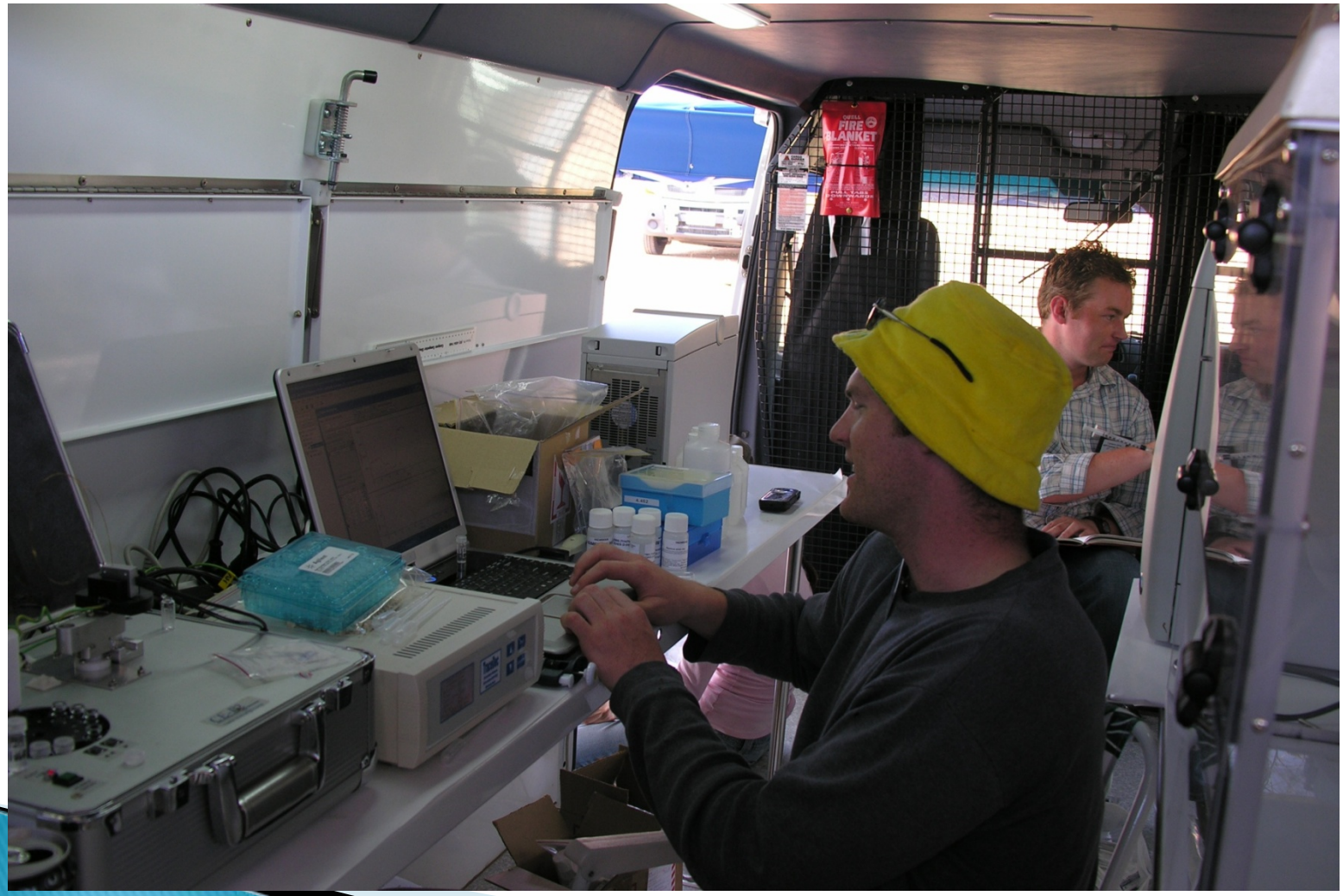
Device	Device Type
D1	$KClO_3$, S, Al
D2	Black powder (KNO_3, S, C)
D3	NH_4NO_3, Fuel Oil
D4	Powermite (NH_4NO_3 slurry)
D5	$KClO_4$, Sugar

- After detonation, residues contain starting materials and numerous oxidation products, as well as background ions

Target Ions

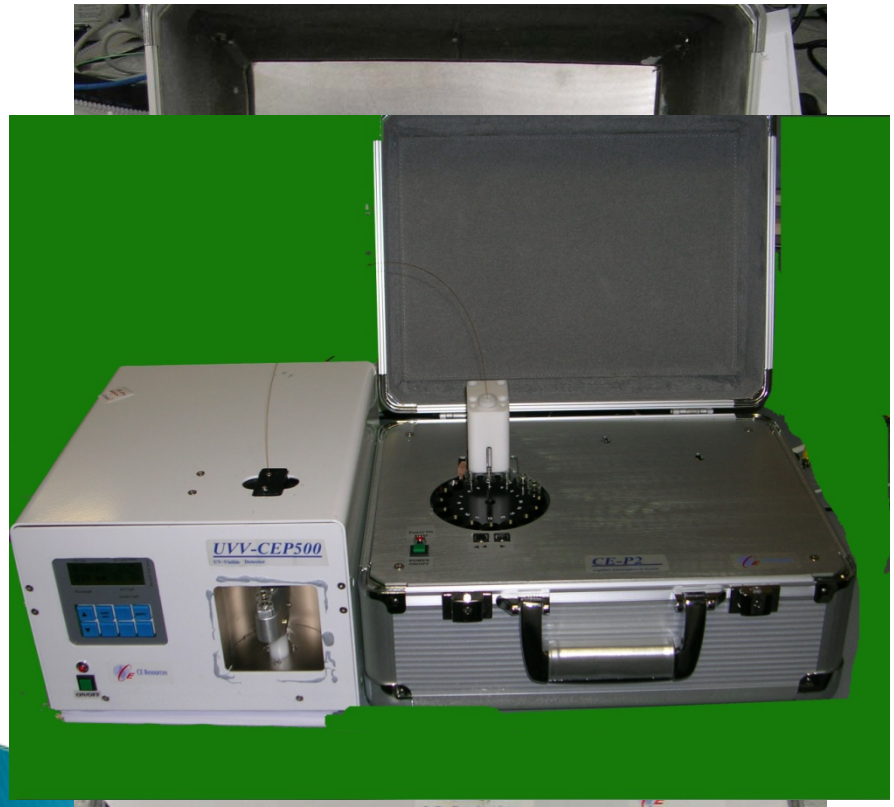
- Anions:
  - F^-, Cl^-, CH_3COO^-, NO_2^-, CNO^-, ClO_3^-, ClO_2^-, $PhCOO^-$, NO_3^-, CO_3^{2-}, SO_4^{2-}, SCN^- , $S_2O_3^{2-}$, PO_4^{3-}, ClO_4^-
- Cations:
  - Na^+, K^+, NH_4^+, $MeNH_3^+$, $EtNH_3^+$, Mg^{2+}, Mn^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Al^{3+}

In-Field Analysis (Mobile Laboratory)



Platform 1: Portable CE

- Commercial CE-P2 from CE Resources (Singapore)
- In attaché case, requires 30 W power, AC/DC operation (3hr battery)
- 16 vial autosampler
- Comes with UV detector, however, many analytes do not absorb UV light

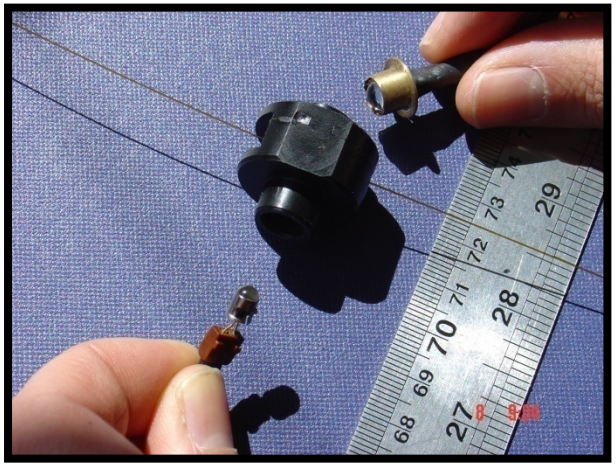


320 mm x 230 mm x 150 mm
3.5 kg (8kg with detector)

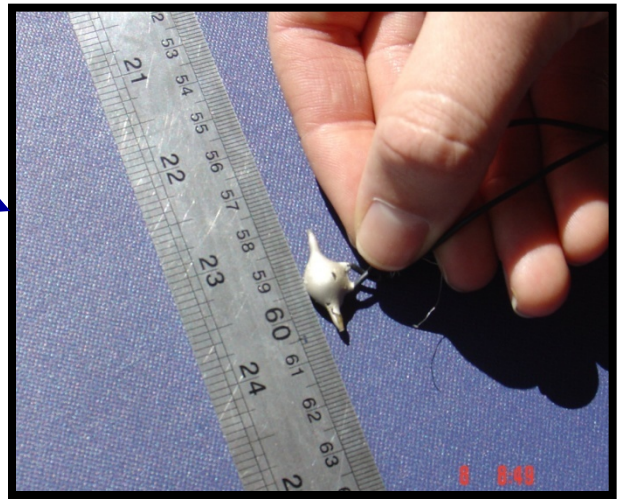
CE Modifications

- Apply in-house and commercial miniaturised detection systems

Optical: LED-based indirect photometric detection



Electrochemical: Contactless capacitively coupled conductivity detection (C^4D)

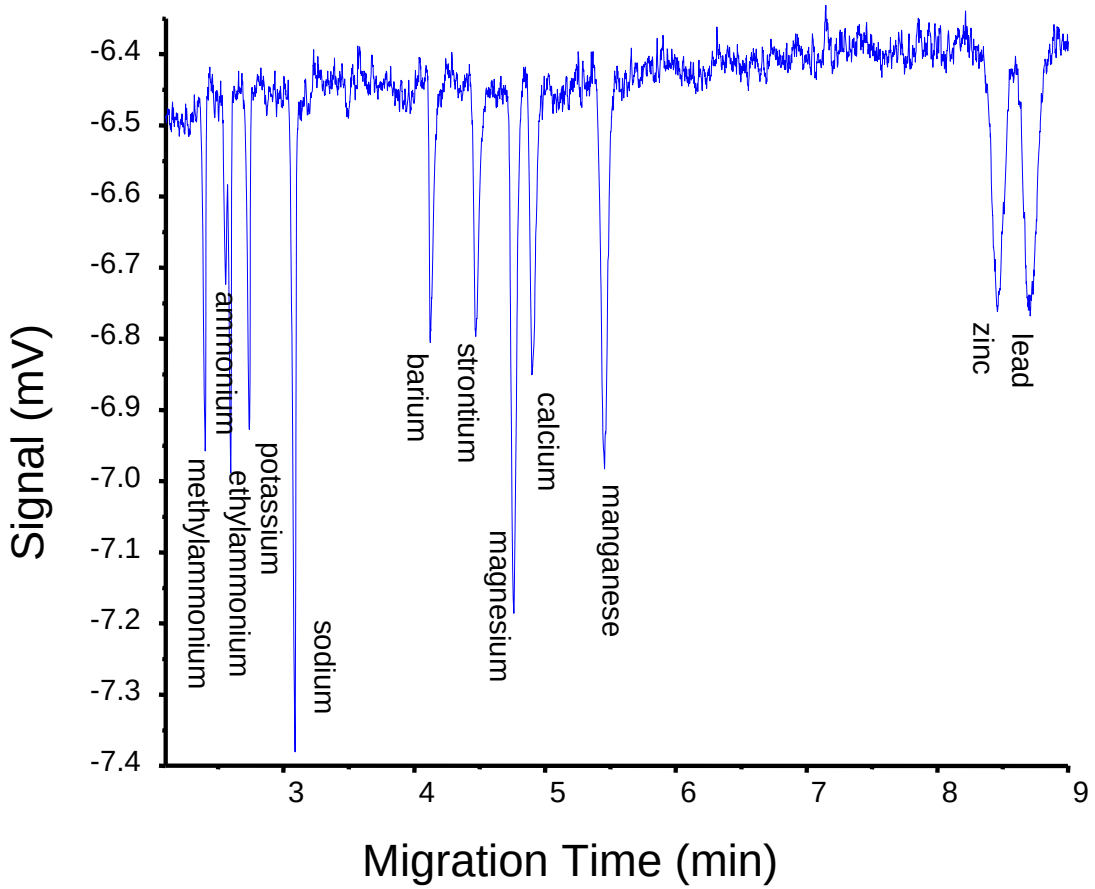


Detection of Cations by CE

- Most cations absorb poorly in the UV–Vis spectrum
- Hence a universal detection system must be adopted (eg indirect photometric or conductivity)

Cation Separation using Chrysoidine

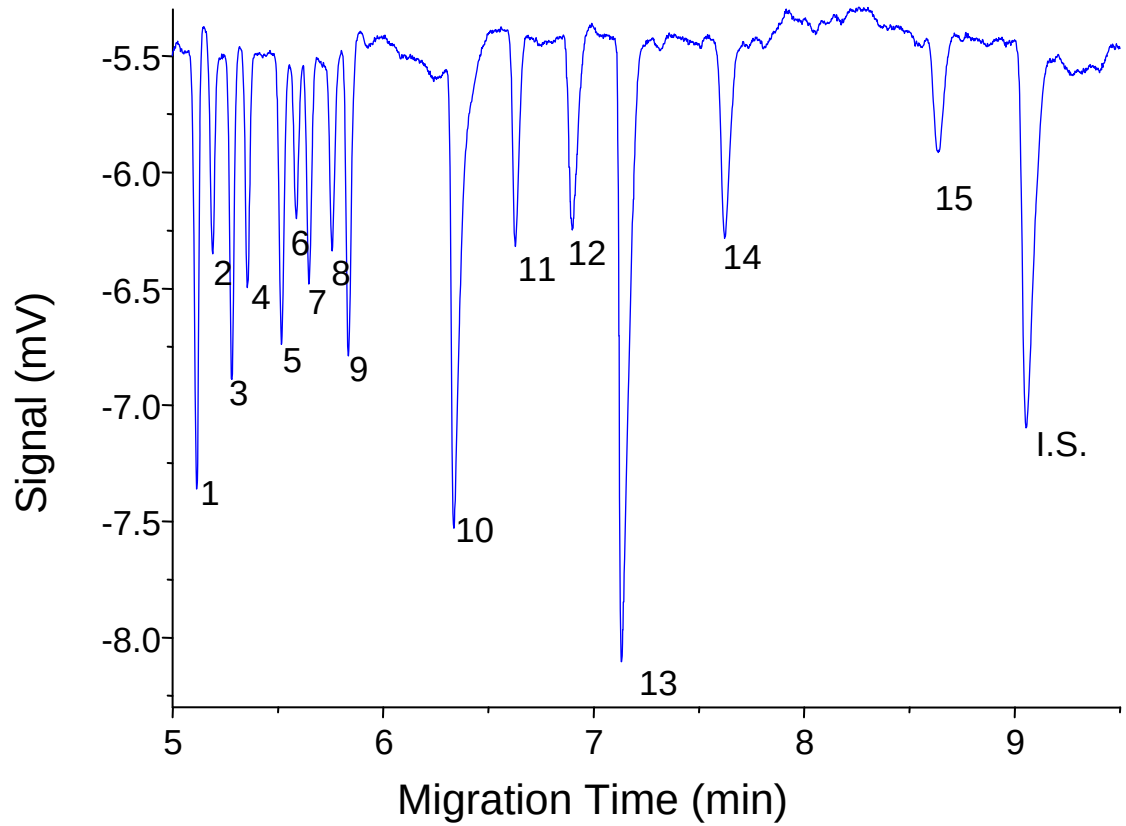
- Indirect photometry at 470 nm using LED light source
- Using methanol greatly improved baseline stability of the CE system
- Removed dye/wall interactions
- 1% acetic acid added as a weak complexation agent



J.P. Hutchinson, C.J. Evenhuis, C.A. Johns, A.A. Kazarian, M.C. Breadmore, M. Macka, E F. Hilder, R.M. Guijt, G.W. Dicinoski and P.R. Haddad, *Anal. Chem.*, 79, **2007**, 7005-7013.

Anion separation with LED Detection

- 10 mM CrO_3, 10 mM Na_2CrO_4, 40 mM Tris in aqueous solution.
- Indirect detection with a 370 nm LED source



Peak identities: **1.** Cl^-, **2.** $S_2O_3^{2-}$, **3.** NO_2^-, **4.** NO_3^-, **5.** SO_4^{2-}, **6.** ClO_4^-, **7.** SCN^-, **8.** ClO_3^-, **9.** CNO^-, **10.** F^-, **11.** ClO_2^-, **12.** PO_4^{3-}, **13.** CO_3^{2-}, **14.** CH_3COO^-, **15.** $C_6H_5COO^-$, **I.S.** hexane sulfonate

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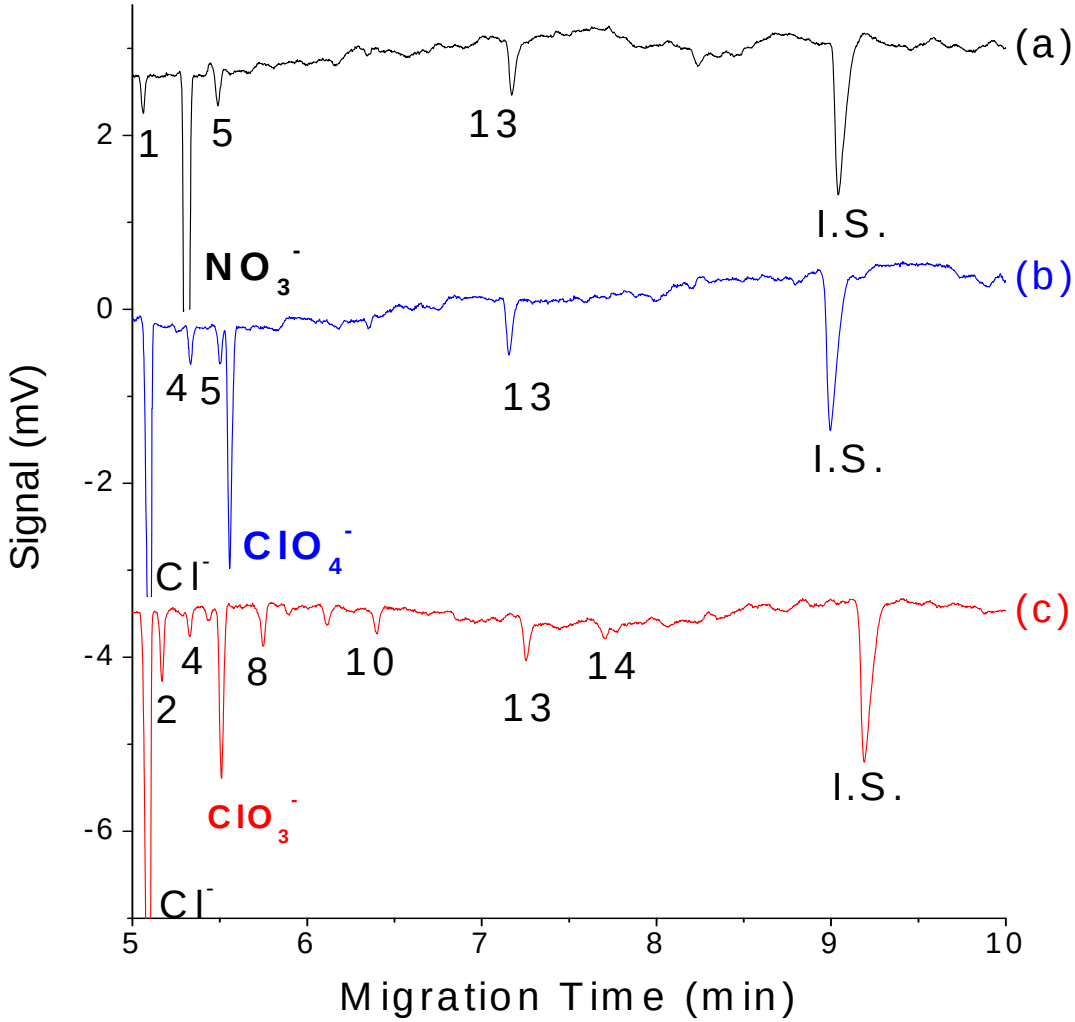
Anions in Post-Blast Residues

(a) ammonium nitrate/fuel oil (ANFO)

(b) potassium perchlorate/sugar

(c) sodium chlorate/ sulfur/aluminium



Analytes:

1.Chloride, 2. thiosulfate, 3. nitrite, 4. nitrate, 5. sulfate, 6. perchlorate, 7. thiocyanate, 8. chlorate, 9. cyanate, 10. fluoride, 11. chlorite, 12. phosphate,13. carbonate,14. acetate, 15. benzoate

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Cations in Post-Blast Residues

(a) ammonium nitrate/fuel oil (ANFO)

(b) potassium perchlorate/sugar

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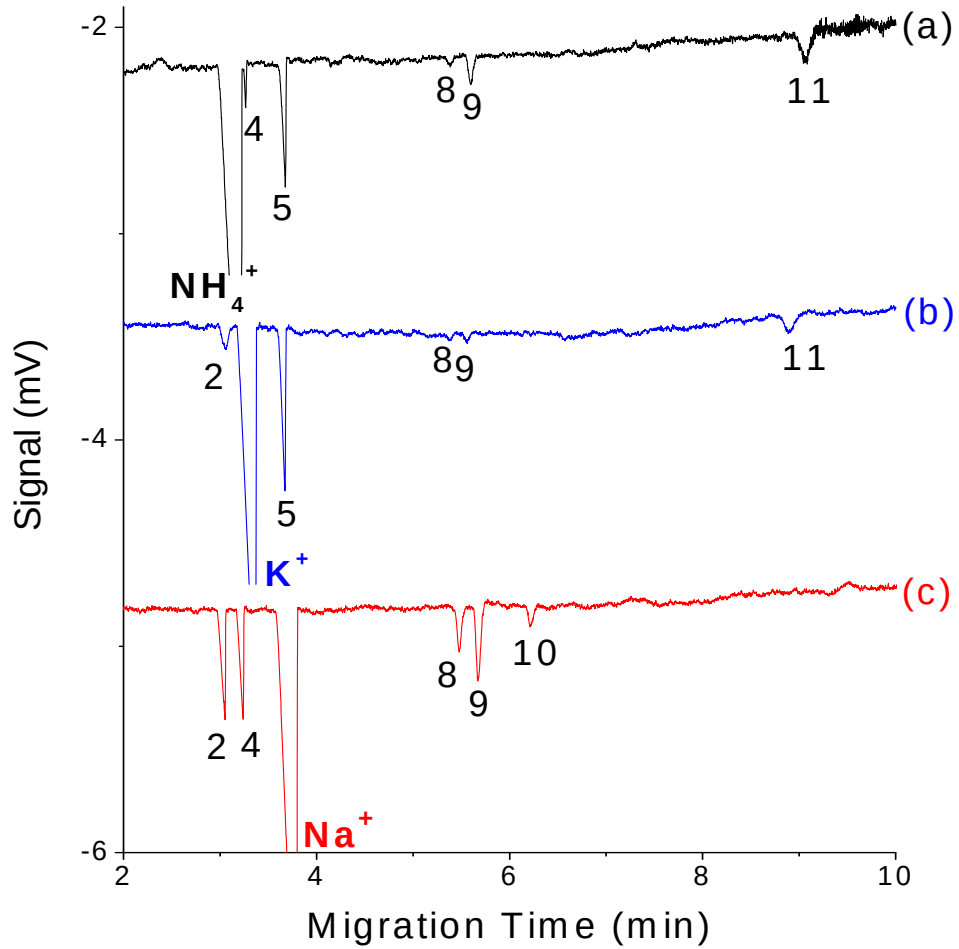

Analytes:

1. Methylammonium, 2. ammonium, 3. ethylammonium, 4. potassium, 5. sodium, 6. barium, 7. strontium, 8. magnesium, 9. calcium, 10. manganese, 11. zinc,12. lead

J.P. Hutchinson, C.J. Eijenhuis, C.A. Johns, A.A. Kazarian, M.C. Breadmore, M. [illegible]ska, E F. Hilder, R.M. Guijt, G.W. Dicinoski and P.R. Ha[illegible]
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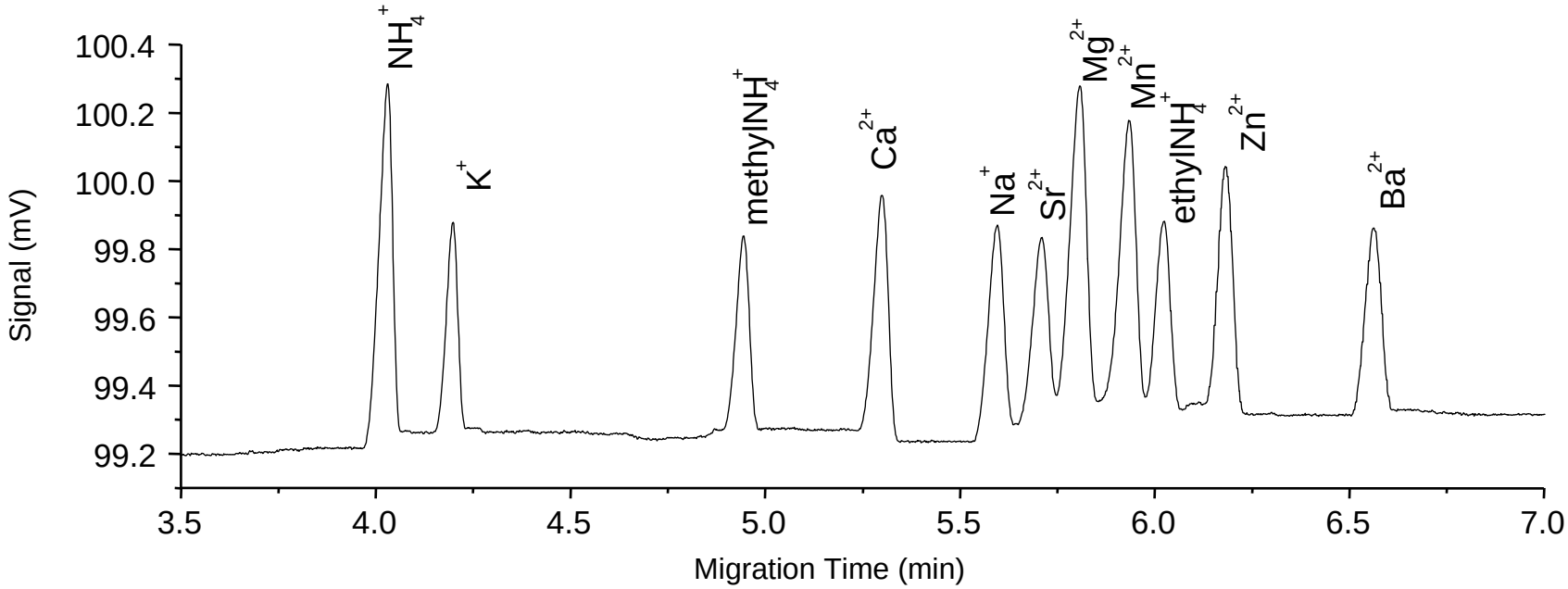
Commercial C^{4}D detector

- Universal detection method
- TraceDec™ produced by ISTECH (Innsbruck, Austria)
- Can be placed anywhere along the capillary
- Provides analogue and digital output
- Power: 30VA 115/230VAC60/50Hz
- Dimensions (H/L/W): 105/250/250mm
- Weight: 3kg
- Operating conditions: 18 to 30°C, 45 to 85% relative humidity
- www.istech.at

Cations by Conductivity Detection



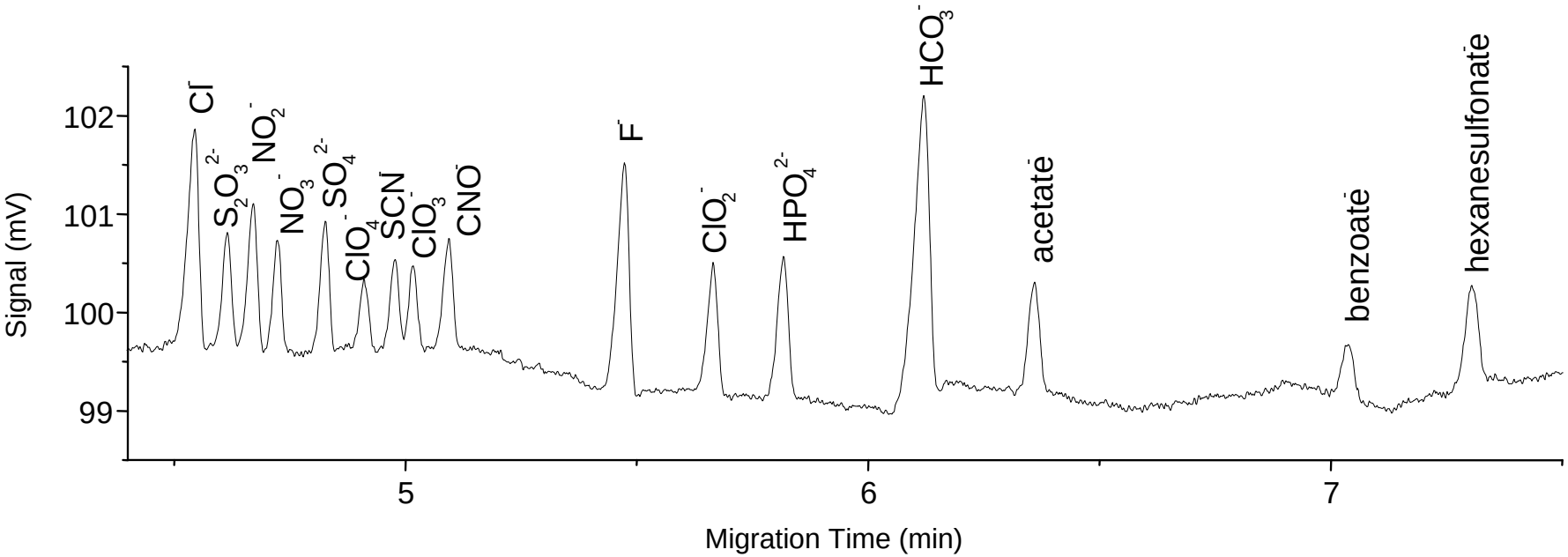
- Cations cannot be separated using electrophoretic mobility alone
- Low conductivity Mes/His buffer at higher pH not capable of separating all cations
- Hence medium conductivity buffer (k=760 mS/cm) acetate/His buffer provided better peak shapes

Conditions:

Capillary:	**75 μm, 73 cm uncoated fused silica**
Sample:	**11 cation mix in Milli-Q**
BGE:	**10 mM histidine, 50 mM acetic acid, 1 mM hydroxyisobutyric acid, 0.7 mM 18-crown-6 ether in aqueous solution, pH 4.1**
Voltage:	**25kV**
Detection:	**TraceDec C^4D**
LOD:	**30-240 ppb**
Efficiency:	**Up to 153,000 plates/m**

C.A. Johns, J.P. Hutchinson, R.[illegible] Guijt, M.C. Breadmore, E.F. Hilder, C. Lennard, G.W. Dicinoski, and P.R. Ha[illegible] *Electrophoresis.*, **2008**, Submitted.

Anions by Conductivity Detection



- Anions can be separated based on electrophoretic mobility alone
- pH of electrolyte important to ensure charge on weak acids
- Ionic strength is optimised to reduce electromigrational dispersion

Conditions:

Capillary:	**75 μm, 90 cm fused silica coated with hexadimethrinebromide**
Sample:	**16 anion mix in milli-Q**
BGE:	**70 mM Tris, 70 mM 2-cyclohexylamino)-ethanesulfonic acid, pH 8.9**
Voltage:	**-25kV**
Detection:	**TraceDec C^4D**
LOD:	**20-200 ppb**
Efficiency:	**Up to 373,000 plates/m**

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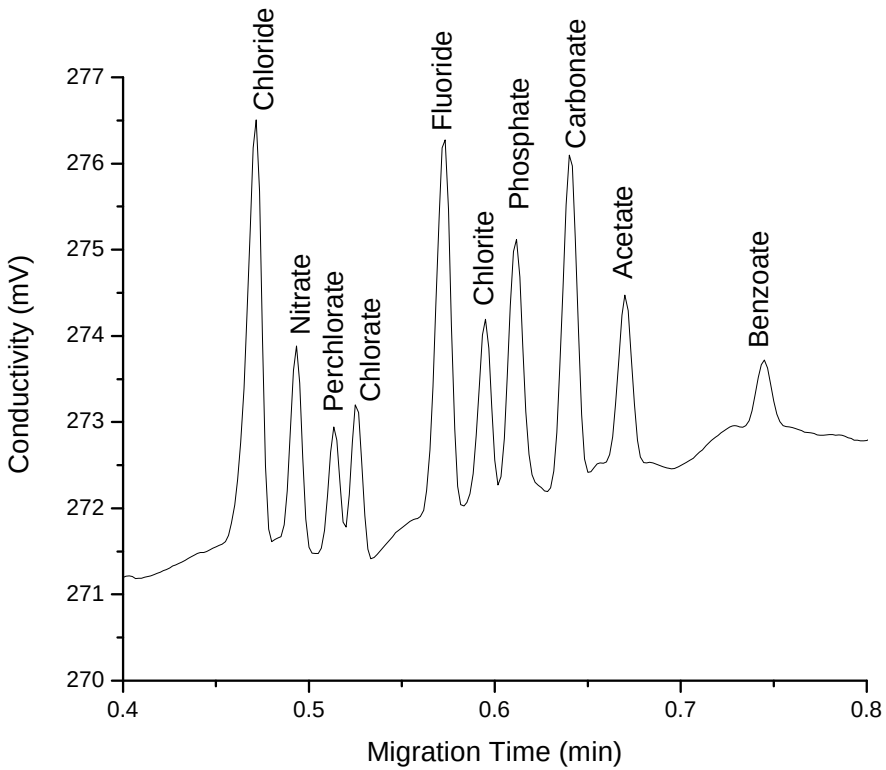
Fast Separation



- Separation in less than 60 seconds
- Very important for screening applications

Conditions:

Capillary:	**75 μm, 30.6 cm fused silica coated with hexadimethrinebromide**
Sample:	**0.5-1.0 ppm 10 anion mix in Milli-Q water injected electrokinetically 5 sec at -1kV**
BGE:	**70 mM Tris, 70 mM 2-cyclohexylamino)-ethanesulfonic acid, pH 8.9**
Voltage:	**-20kV**
Detection:	**TraceDec C^4D at 24.5 cm from injection point**

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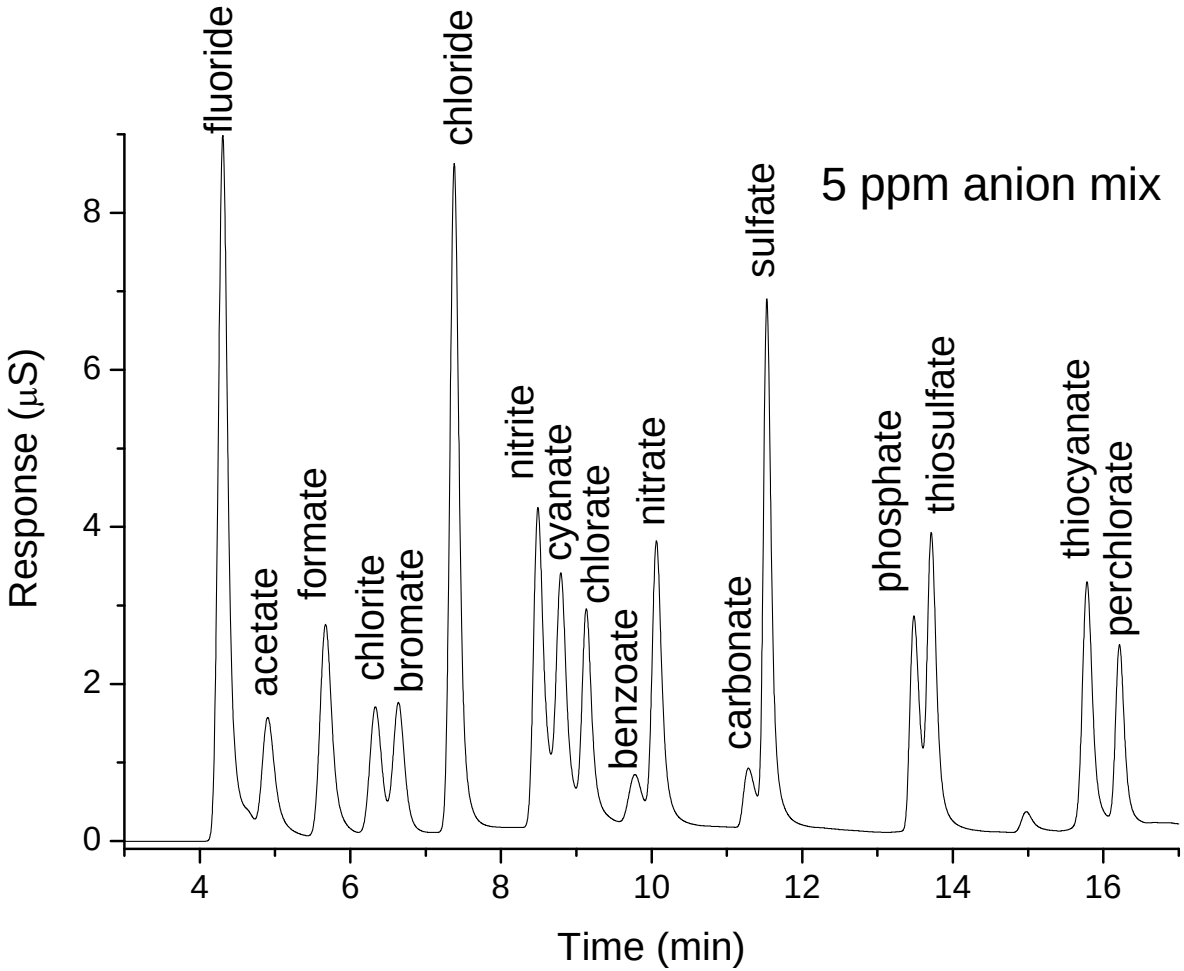
Platform 2: Microbore IC system

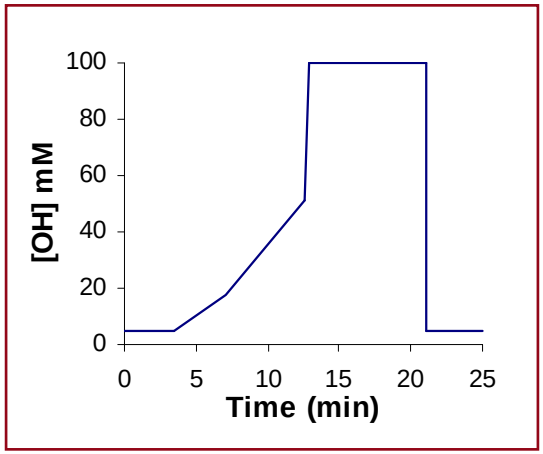
- Dual ICS-2000 system
  - Simultaneous anion and cation analysis
- Employs a 2mm i.d. x 250mm column
- Suppressed conductivity detection
- Amenable to field-deployment

Anion Separation on Dionex AS20



Conditions:

- 2 x 250 mm AS20 Dionex column
- **0.375 mL/min flow rate**
- 35°C, 5 µL sample injection
- ASRS II 2 mm suppressor @ 100 mA
- **Eluent:** Hydroxide gradient shown below



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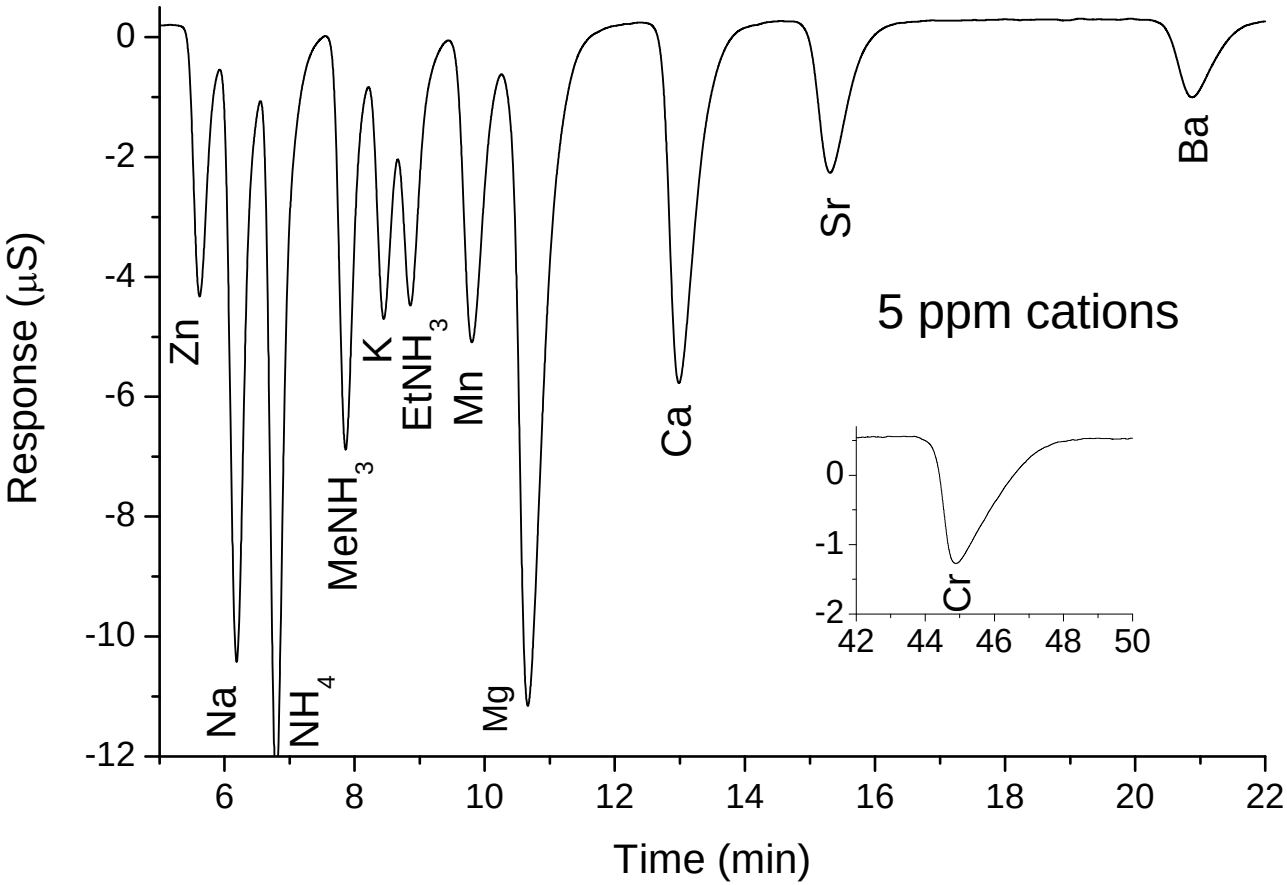
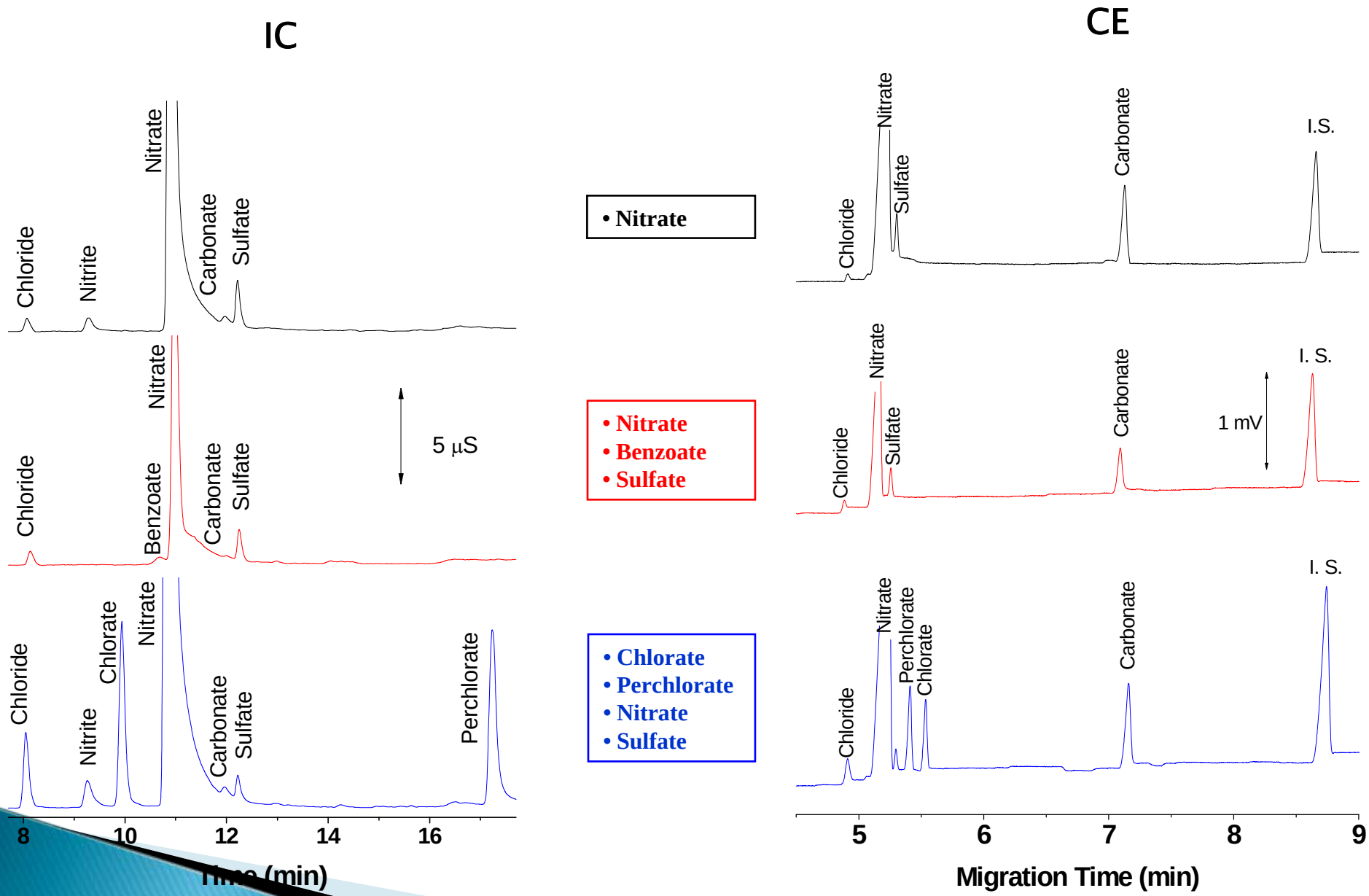
Cation Separation on Dionex SCS-1



Conditions:
- 2 x 250 mm SCS-1 Dionex column
- 0.25 mL/min flow rate
- 30° C, 5 μL sample injection
- Non-suppressed conductivity detection
- **Eluent:** 5.25 mM oxalic acid,1% acetonitrile

C.A. Johns, R.A. Shellie, O.G. Potter, J.W. O'Reilly, J.P. Hutchinson, R.M. Guijt, M.C. Breadmore, E.F. Hilder, G.W. Dicinoski and P.R. Haddad, *J. Chrom. A.*, 1182, **2008**, 2005.

Witness Plates– Anions



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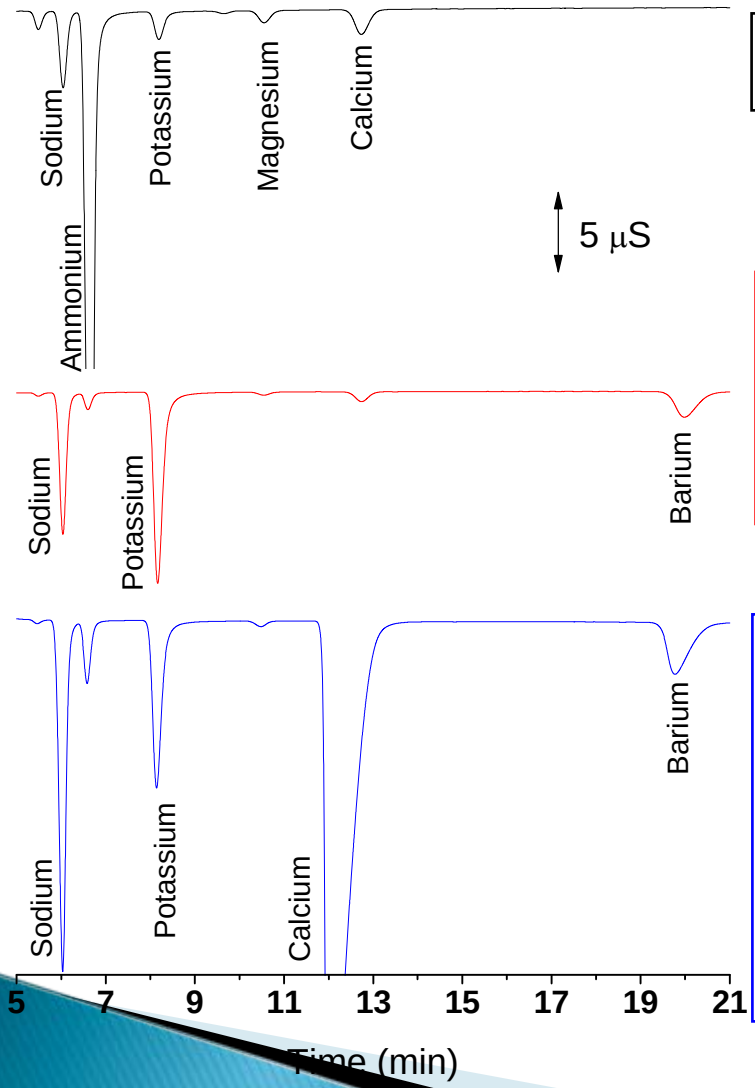
Witness Plates– Cations

IC



ANFO (300g)
AN:Diesel ratio 16:1

- **Ammonium**

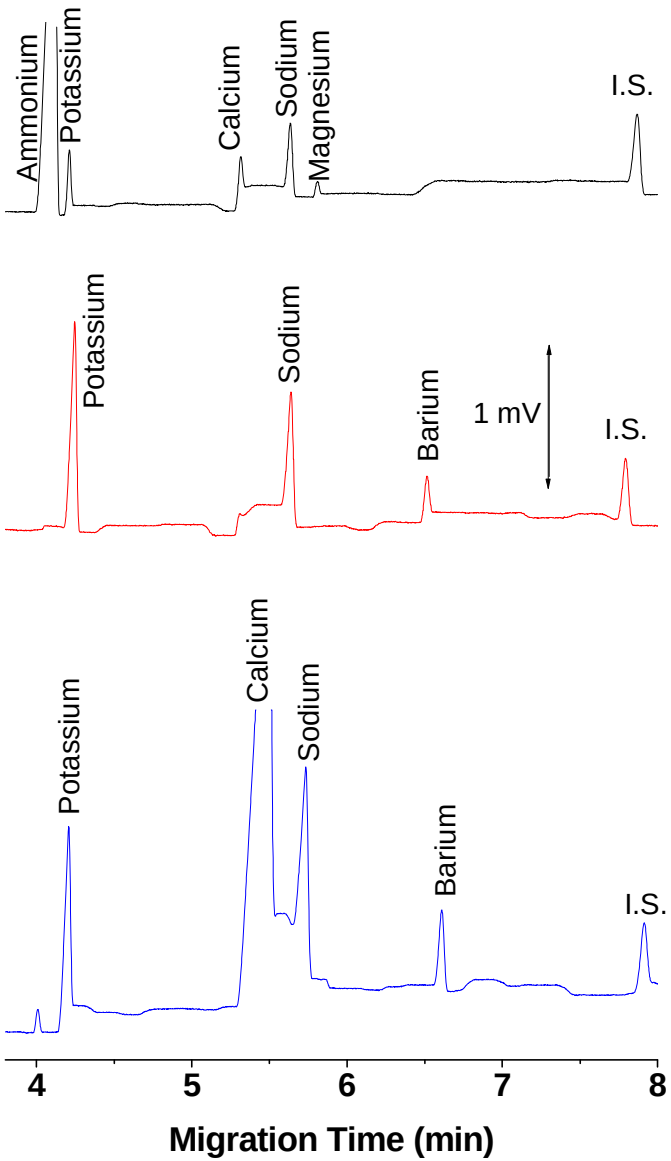
Black Powder (325 g)
165 g potassium nitrate
60 g barium nitrate
30 g sulfur
45 g charcoal
25 g sodium benzoate

- **Potassium**
- **Sodium**
- **Barium**

Chlorate/Perchlorate/ Nitrate/sulphur/ charcoal (250g)
40 g barium nitrate
80 g calcium nitrate
30 g sodium chlorate
40 g potassium perchlorate
25 g sulfur
35 g charcoal

- **Potassium**
- **Sodium**
- **Calcium**
- **Barium**

CE



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Pre-Blast Project

Pre-Blast Project Team

- Collaborating Organisations:
  - Dionex Pty Ltd/Corporation
  - Australian Federal Police (AFP)
  - Australian Customs Service
  - National Institute for Forensic Science (NIFS)
  - Forensic Science South Australia (FSSA)
  - Victoria Police
  - Department of Transport and Regional Services (DOTARS)
  - Tasmanian Police
  - Qantas

Pre-Blast Project Overview

- To develop rapid analytical techniques for the pre-blast identification of inorganic and peroxide based improvised explosive devices (IEDs).
- Current detection methods use chemical spot tests
- Develop in-field instrumentation based on CE and IC

Screening Process (CE) (<30 sec) → Confirmatory Analysis (IC) (< 5 mins)

- Applications: screening people at points of entry and airports, suspect packages, vehicles, crime scenes, cars, shipping containers, identification of unexploded devices, forensic pre-blast testing, etc.

Pre-Blast Project Approach

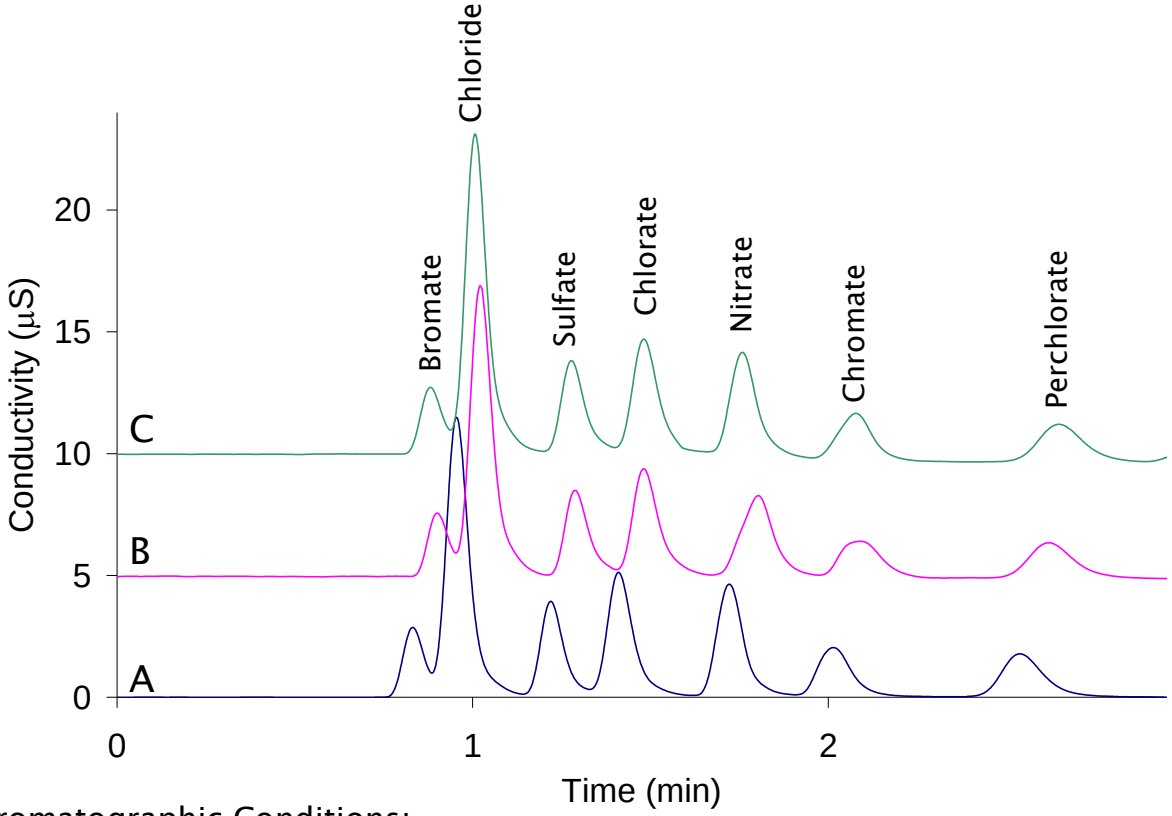
- Alert and separation protocols will be in the order of sub-30 seconds to 5 minutes respectively
- Fast, front-line alert protocol using a short capillary CE
- The separation technique would be performed in an adjoining room using a complimentary fast IC
- Instruments will employ a specialised sample introduction system with push-button initiation and audio-visual display
- The system will able to be operated by a person with little or no training in IC and CE.
- The instrumentation would run continuously in a stand-by mode, with a daily calibration, and require monthly servicing by a technician

Pre-Blast Project Approach

- Based upon common IEDs the alert swab and the analytical protocol should be able to identify the presence of the following ions:
  - Bromate (BrO_3^-); Chlorate (ClO_3^-); Nitrate (NO_3^-); Perchlorate (ClO_4^-); Chromate (CrO_4^{2-}); Sulfate (SO_4^{2-}); Chloride (Cl^-); and Peroxides
- Swabbing procedures will be optimised
- Desorption processes and sample introduction methods will be be developed
- Background levels on these ions will be determined
  - Threshold values identified to prevent false positives/negatives

Fast Ion Chromatography

- Comparison of columns packed under identical conditions



Chromatographic Conditions:
Self-packed 4 x 30 mm AS20 columns
Flow = 1.8 ml min^{-1}, Temp = 30°C, Sample injection volume = 25 µL, Detection = suppressed conductivity (ASRS ULTRA II 4 mm, current 168 mA), Sample 5 mg L^{-1} anion mix
* Gradient profile: 5 mM from 0.0 to 0.5 min, 5–10 mM from 0.5 to 1.1 min, 10–30 mM from 1.1 to 2.0 min, 30 mM from 2.0 to 2.5 min, 5 mM from 2.5 to 3.5 min.

E. Tyrrell, E.F. Hilder, G.W. Dicinoski, R.A. Shellie, M.C. Breadmore, and P.R. Haddad, *J. Chrom. A.*, **2008**, Submitted.

Conclusions

- Portable CE provides separation of all target anions and cations and reliable fingerprinting of explosive residues.
  - Features are:
    - Portability of instrumentation
    - In-field use
    - Speed
- IC also provides good separation and fingerprinting.
  - Features are:
    - Sensitivity
    - Current instrument only at bench-top scale
    - Field-deployable and applicable to mobile laboratory analyses
    - Robust and rugged operation
    - Complimentary and confirmatory analyses with Portable CE

Acknowledgements

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- Australian Research Council (ARC, LP0669302)
- Dionex Corporation
- Australian Federal Police (AFP)
- Australian Customs Service (ACS)
- National Institute for Forensic Science (NIFS)
- Forensic Science South Australia (FSSA)
- Victoria Police
- Department of Transport and Regional Services (DOTARS)
- Tasmanian Police
- eDAQ
- CE Resources
- ACROSS members and visitors
  - Pavel Kuban, Peter Hauser, Katrina Munting, Sam Poynter, Tim Causon, Carrie-Anne Bloomfield

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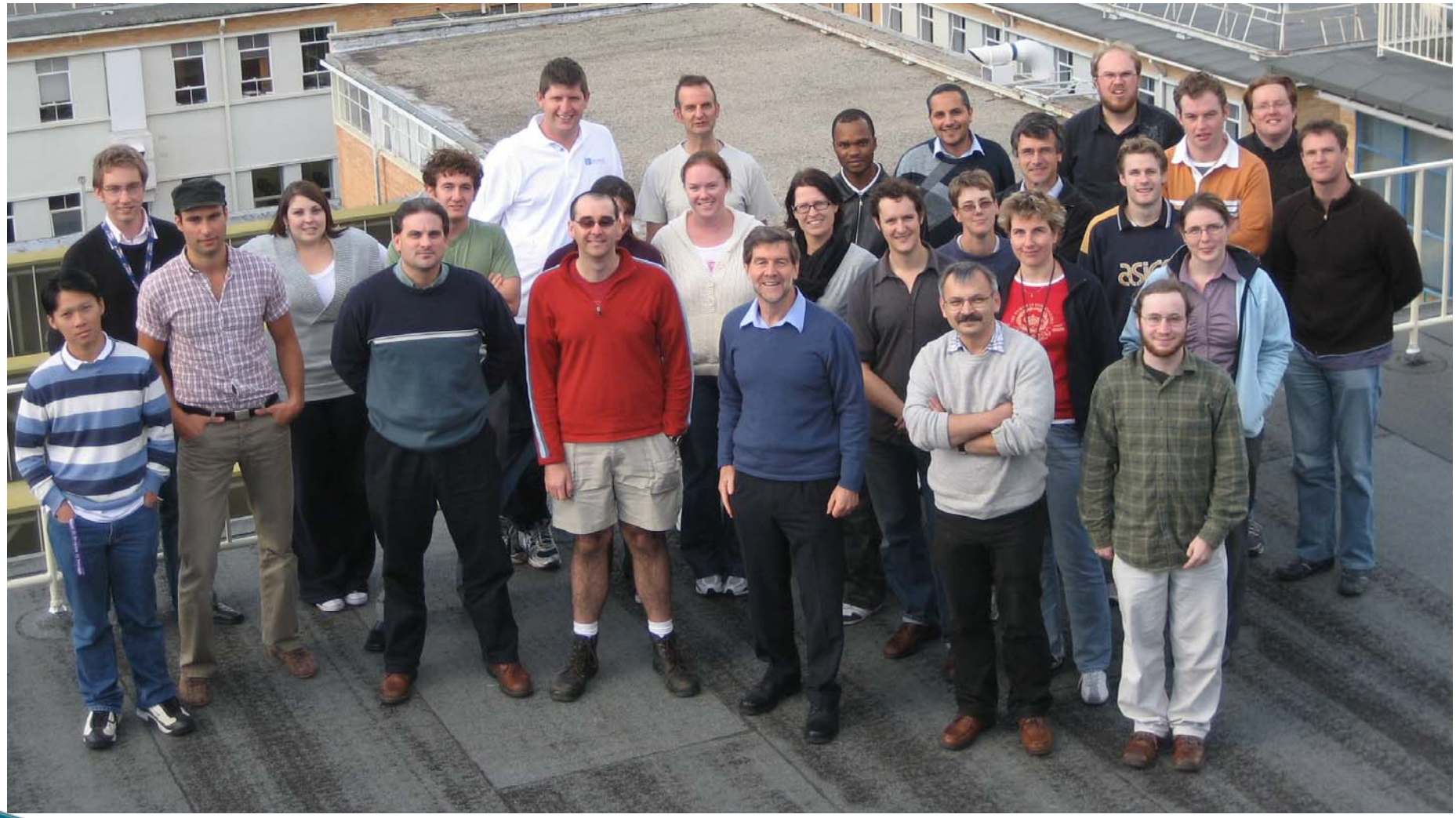

Thank you