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Joint ICTP/IAEA Workshop on Advanced Simulation and Modelling for Ion Beam Analysis

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Ambiguity: Using Multiple Techniques

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Ambiguity: Using Multiple Techniques

Joint ICTP/IAEA Workshop on Advanced Simulation and Modelling for Ion Beam Analysis
23 - 27 February 2009, Miramare - Trieste, Italy

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Guildford, England

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International Atomic Energy Agency

Contents

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- Ambiguity in principle: Alkemade's (N-1)
- The centrality of the collected charge
- What the spectrum tells you
- Demonstrable ambiguity: Butler & chemical priors
- Molecules
- Multiple spectra

Previous Work

Two contributions at the 1989 IBA Conference, Kingston, Canada

- **Alkemade** P F A, Habraken F H P M and van der Weg W F, 1990: On the ambiguity in the analysis of Rutherford backscattering spectra *Nucl. Instrum. Methods* B **45** 139–42

  Shows that spectra are less ambiguous than one might think: if there are N elements in the sample you need N-1 independent spectra for solution

- **Butler** J W, 1990: Criteria for validity of Rutherford scatter analysis, *Nucl. Instrum. Methods* B **45** 160–5

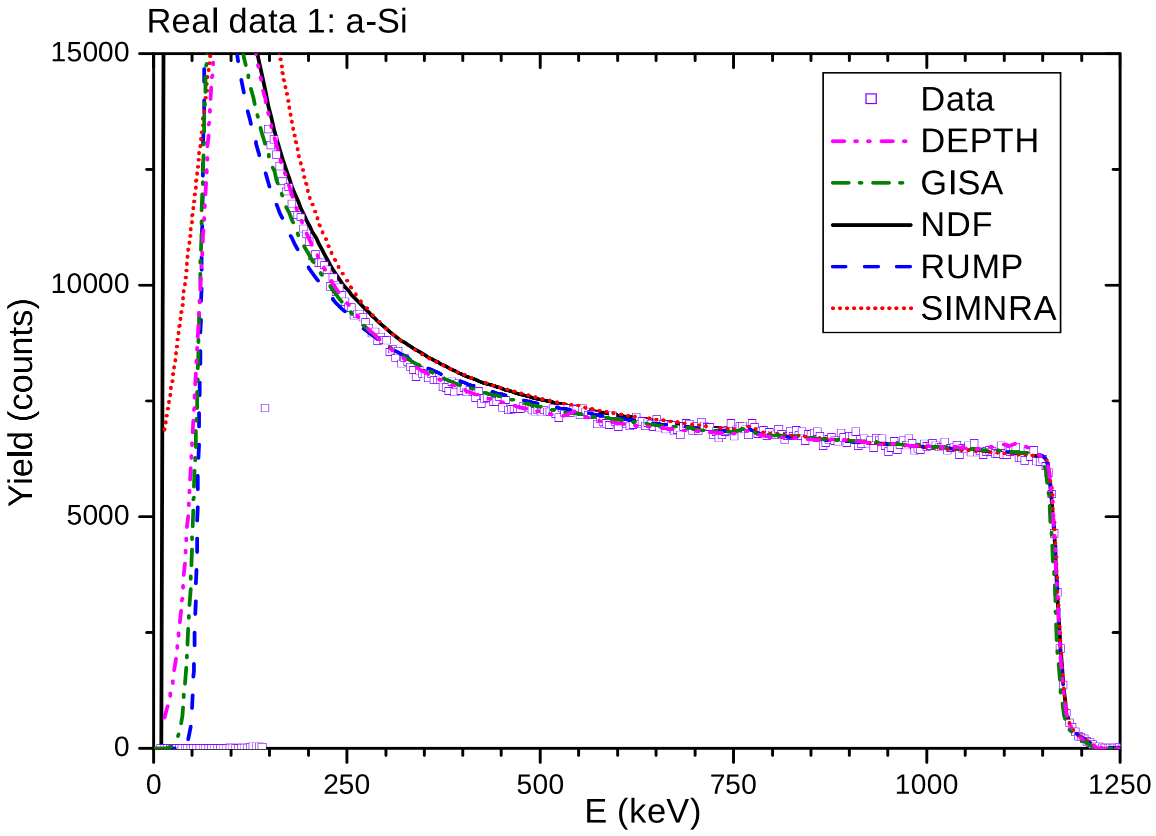
  Shows that there are some strictly ambiguous spectra, but that chemical prior knowledge imposed on the data can enable an unambiguous solution

These are discussed in detail in:

- C Jeynes, N P Barradas, P K Marriott, G Boudreault, M Jenkin, E Wendler and R P Webb, 2003: Elemental thin film depth profiles by ion beam analysis using simulated annealing—a new tool, J. Phys. D: Appl. Phys. 36 (2003) R97–R126 (Topical Review)

Real RBS Spectrum of a-Si

a-Si, 2MeV, 3.840(8)keV/ch, 1.95(2)msr,
150.0(2)^0 scattering angle, 46.0(5)μC



$A_A = Q\, N_A\, \sigma'_A\, (E, \theta)\ \ \Omega$

$Y_{0,A} = Q\, f_A\ \ \sigma'_A\ \ \Omega\, \Delta\, /\, [\, \varepsilon_0\,]\, _A{}^{AB}$

Doesn't tell us:

Energy, gain Δ

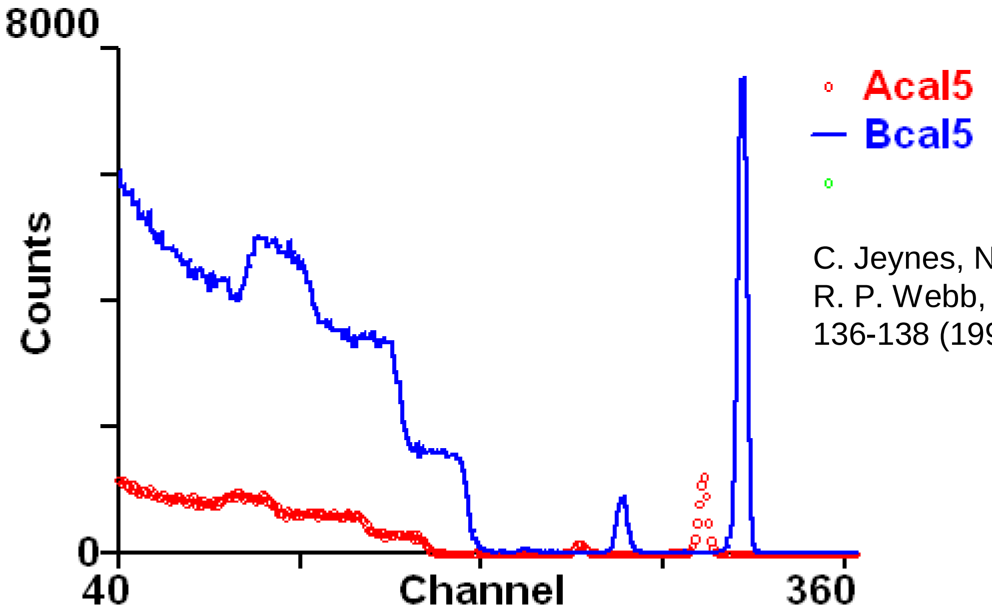
BUT: given [ε] , E, Δ

it does tell us Q*Ω

G. Lulli, E. Albertazzi, M. Bianconi, G.G. Bentini, R. Nipoti, R. Lotti, Nucl. Instrum. Methods B170 (2000) 1.

Electronic Gain

(see detailed treatment in Pitfalls **II**)



C. Jeynes, N. P. Barradas, M. J. Blewett, R. P. Webb, Nucl. Instr. and Meth. B 136-138 (1998) 1229

- what is ambiguous here?
- Energy!
- offset is fitting parameter

Charge Ambiguity

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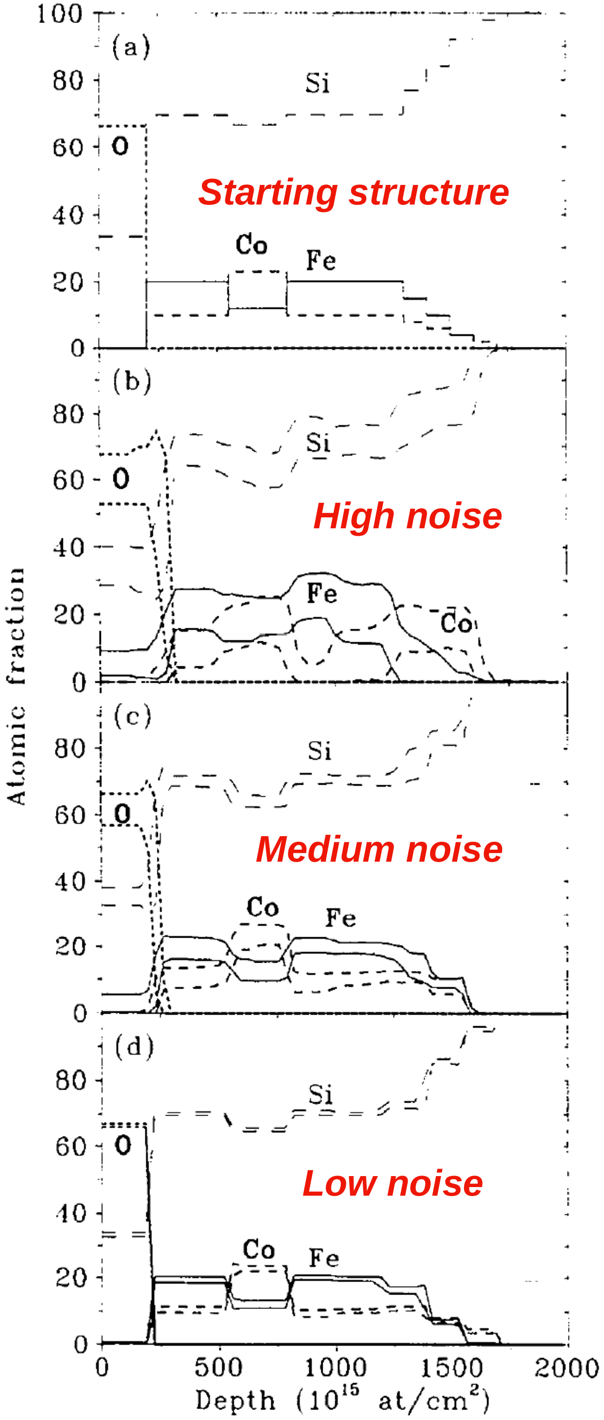
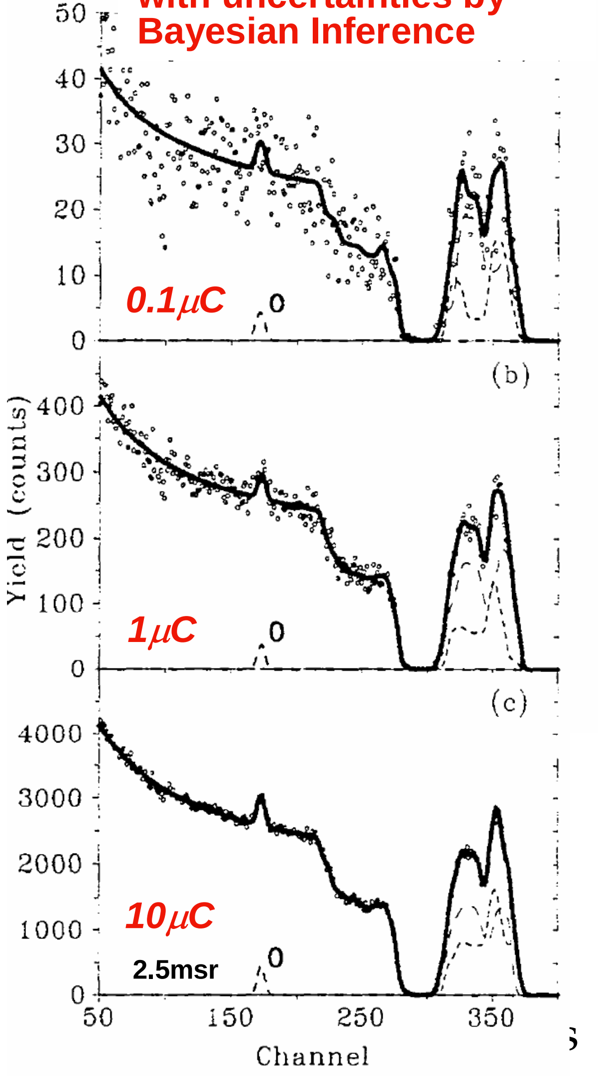


Simulated Annealing fits with uncertainties by Bayesian Inference



You don't need as much collected charge as you might have thought !!

Microbeam RBS analysis works fine !!

Barradas N P, Jeynes C, Jenkin M and Marriott P K, 1999, Bayesian error analysis of Rutherford backscattering spectra, *Thin Solid Films* **343–344** 31–4

Effect of unknown charge

in RBS/PIXE/PIGE analysis of FeCo borosilicide on oxidised Si

(self-consistent analysis by NDF)

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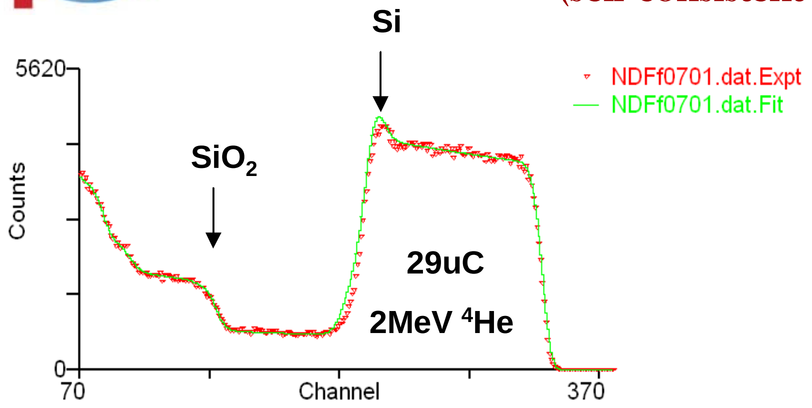
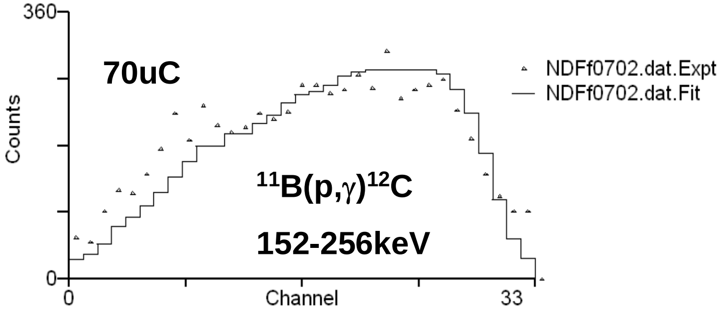
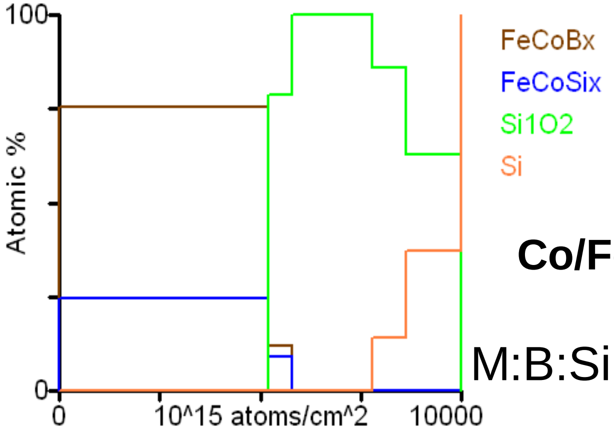
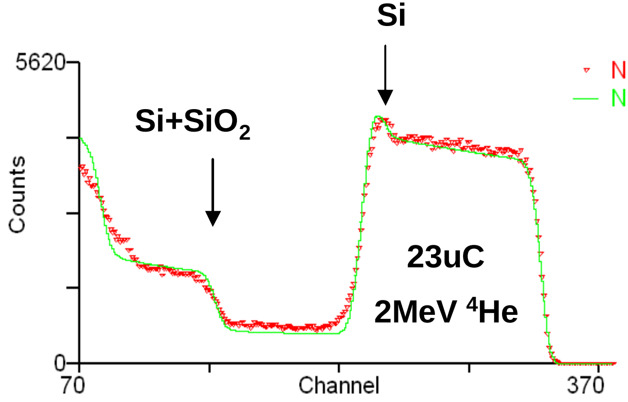


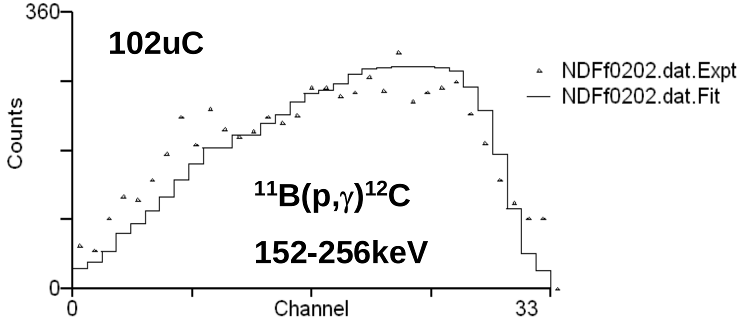


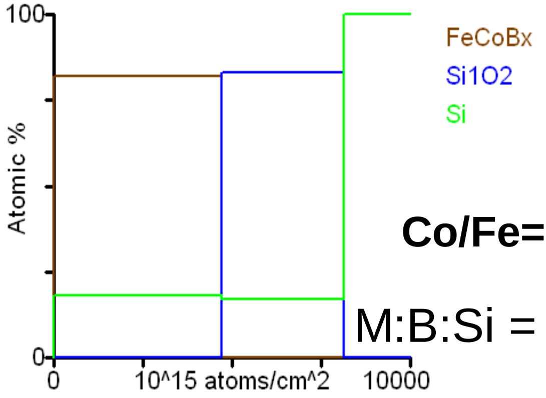


Co/Fe=3.8 (PIXE)

M:B:Si = 26:58:16





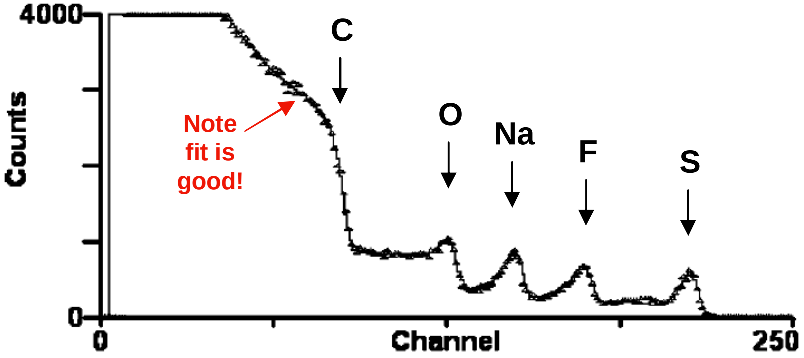


Co/Fe=3.8 (PIXE)

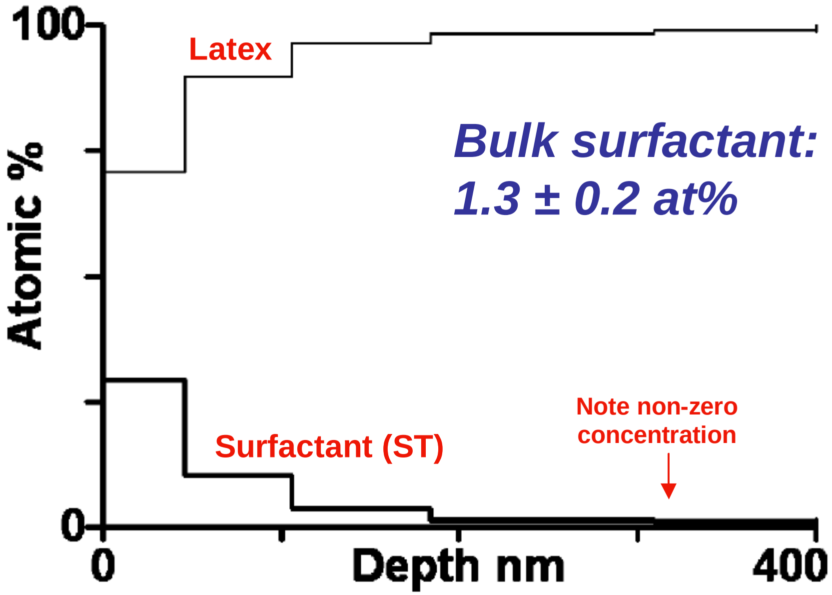
M:B:Si = 37:45:18

Charge Ambiguity

W.P.Lee, V.R.Gundabala, B.S.Akpa, M.L.Johns, C.Jeynes, A.F.Routh, *Distribution of Surfactants in Latex Films: an RBS study*, Langmuir 2006, 22, 5314-5320



Note fit is good!



Bulk surfactant: 1.3 ± 0.2 at%

Note non-zero concentration

Latex=poly(butyl acrylate *co* styrene)

Applications: water-based gloss paint, glue etc

Surfactant= SDS, SOS, LiDS, ST

Nominal compositions:

Latex: (C,H,O) = (390,520,52)

SDS: (C,H,O,S,Na) = (12,25,4,1,1)

SOS: (C,H,O,S,Na) = (8.17,4,1,1)

LiDS: (C,H,O,S,Li) = (12,25,4,1,1)

ST: (C,O,S,Na,F) = (1,3,1,1,3)

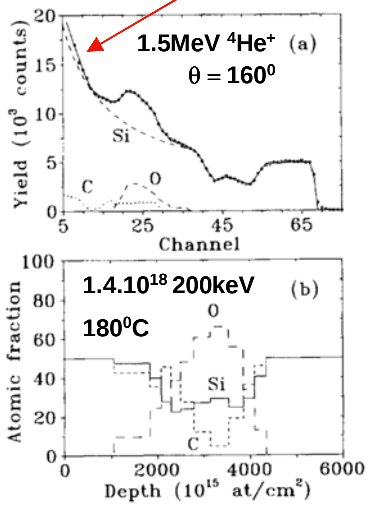
Interest is in the equilibrium near-surface (1μm) concentration of surfactant, to explore the models of drying

The low energy RBS signal had to be used to obtain the composition (the latex:surfactant ratio). The spectra had to be handled *very precisely*

Marangoni flow instabilities → large lateral inhomogeneity (~50 spectra)

Charge Ambiguity

Force
low energy
signal to fit

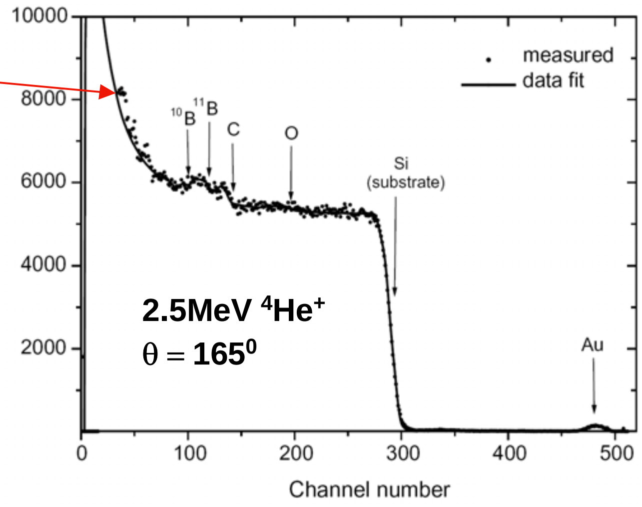


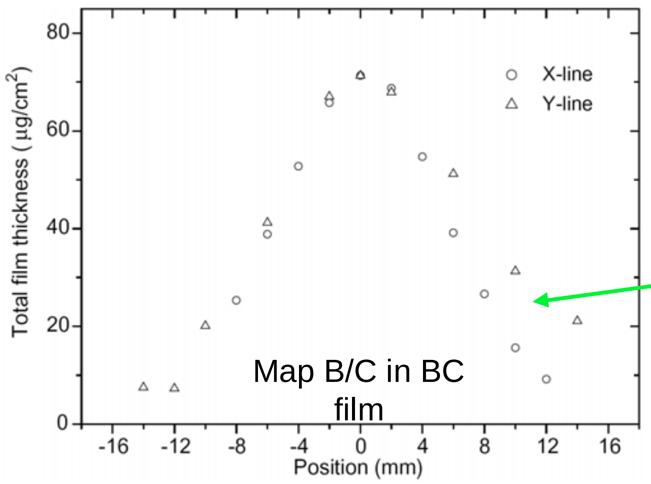
N.P.Barradas, C.Jeynes, S.M.Jackson,

RBS/simulated annealing analysis of buried SiCO$_x$ layers formed by ion implantation of O into cubic silicon carbide,

NIM B136–138, 1998, 1168–71

Form buried oxide in SiC





A.Simon, T.Csákó, C.Jeynes, T.Szörényi, *High lateral resolution 2D mapping of the B/C ratio in a boron carbide film formed by femtosecond pulsed laser deposition*, NIM B249, 2006, 454–457

Great precision can be obtained if proper care in fitting the data is taken

Using background fitting method of Barradas, Jeynes & Jackson

Then light elements can be quantified with confidence, even by RBS alone

Many repeated measurements
+ unifom analytical procedure
= *internal consistency*

Therefore:
procedure valid!

Spectral Ambiguity

- Average Z is ***determined*** by the charge.solid angle product (“charge”) –-- it’s ***not*** a free parameter!
- Invisible elements usually have quite small energy loss and are therefore ***very sensitive*** to the exact value of the charge
- Charge is generally ***not*** very well determined and therefore the invisible elements are ***not well determined***
- Small errors in the charge can give very ***large errors*** in invisible elements
- Spectra from complex samples are frequently very hard to determine the charge from and therefore very ***easy to misunderstand***
- Obtaining ***direct*** information from the “invisible” elements (i.e. making them visible) reduces scope for error.

Spectral Ambiguity

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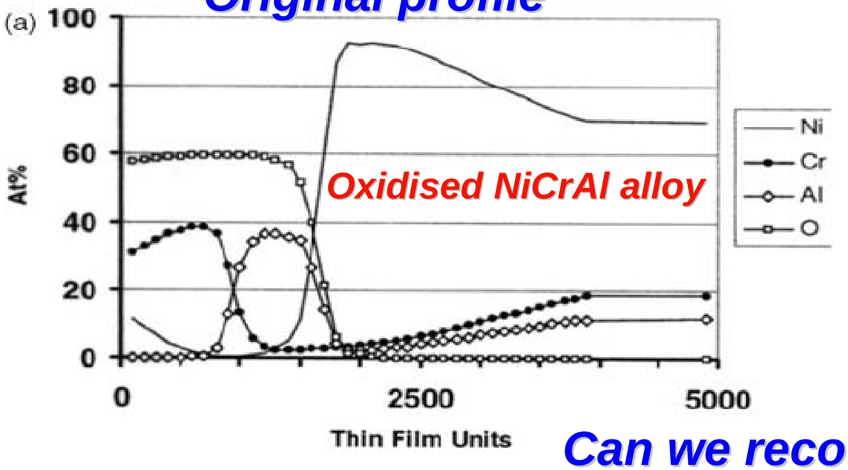
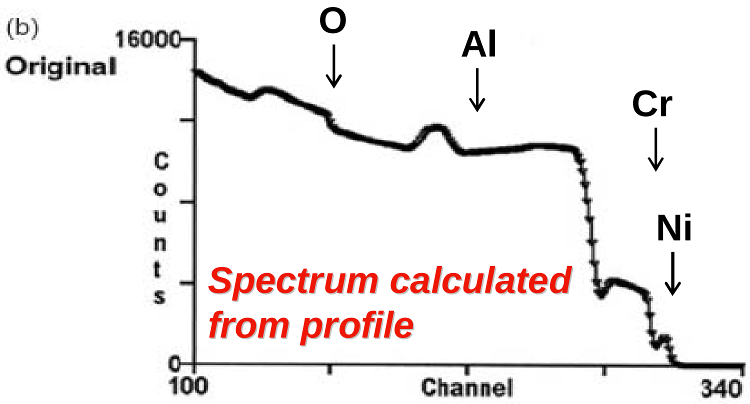
Original profile

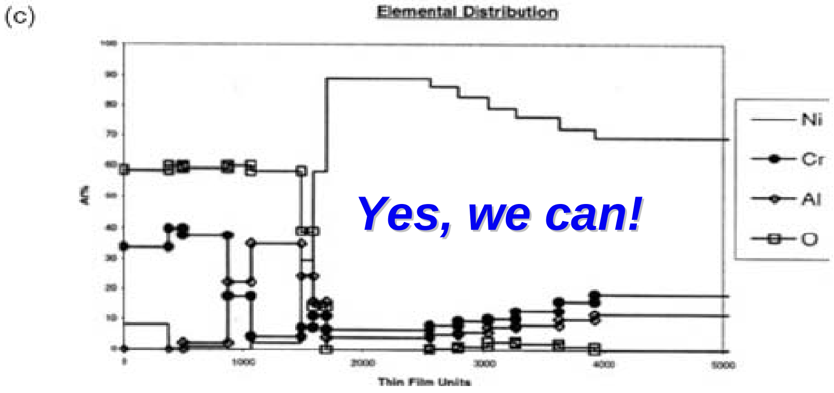


Oxidised NiCrAl alloy

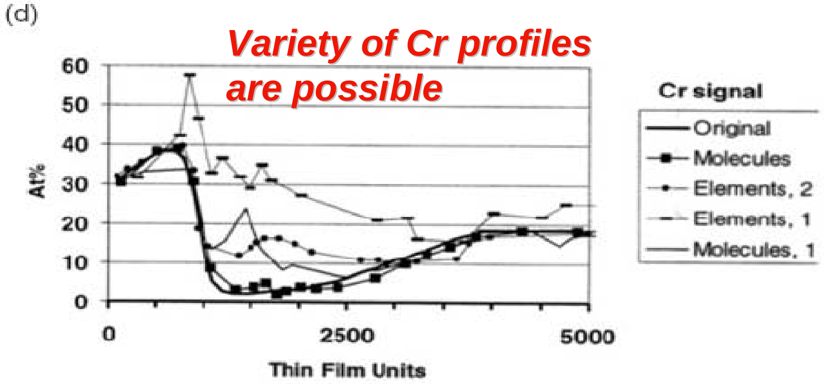


Spectrum calculated from profile

Can we recover the profile from the spectrum?



Yes, we can!



Variety of Cr profiles are possible

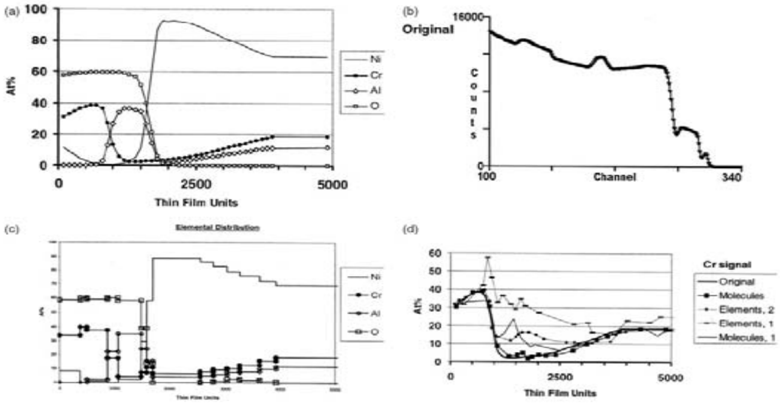
But not unambiguously!

Re-analysis of an oxidized NiCrAl alloy

(following J.W.Butler, *Criteria for validity of RBS analysis,* NIM B45, 1990, 160-165)

Figure is reproduced from Jeynes *et al* J.Phys.D: Appl.Phys. 36, 2003, R97-R126

Spectral Ambiguity



Re-analysis of an oxidized NiCrAl alloy (Butler 1990)

(a) Original profile from which the spectrum was calculated
(b) Spectrum (symbols) and fit (line)
(c) Atomic profile fitted to data assuming molecules and complete oxidation from the surface, using two spectra at different detector angles, and excluding alumina from the surface
(d) Comparison with the original profile of the Cr profile calculated under various assumptions

IBA spectra are inherently ambiguous and there exist multiple valid solutions

- Specifying only elements barely constrains the profile, and even with two detectors the profile is not recovered at intermediate depths.
- Using only one detector with the assumption of molecules is also not sufficient.
- Molecules used are NiO, Cr2O3, Al2O3 and (Ni195 Cr186 Al119).

Occam's Razor: ***non sunt multiplicanda entia praeter necessitatem***
("minimise your assumptions")

Wiiliam of Occam
(c1285-1347?)

Spectral Ambiguity

To avoid ambiguity in Butler's example we needed

- The stated molecules present
- *Only* oxides at the surface
- *No* O in substrate
- Al *excluded* from near-surface region
- Multiple spectra (not mentioned explicitly by Butler)

- The spectra are *systematically* ambiguous
- That is, a variety of solutions we know to be *wrong* are nevertheless perfectly *valid.*

Wiiliam of Occam (c1285-1347?)

A bad fit means that:

you have an *invalid* (an incorrect) solution

A good fit means that:

you have a *valid* solution

but not necessarily a *correct* one!

Molecules *contra* Ambiguity
Rutherford BackScattering

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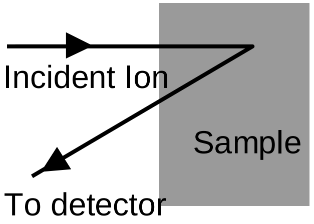
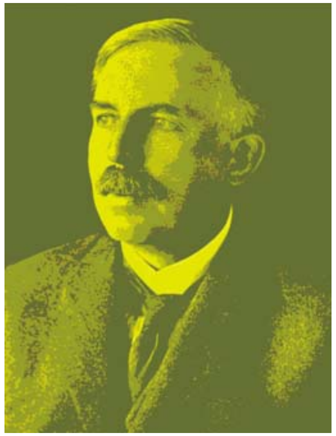
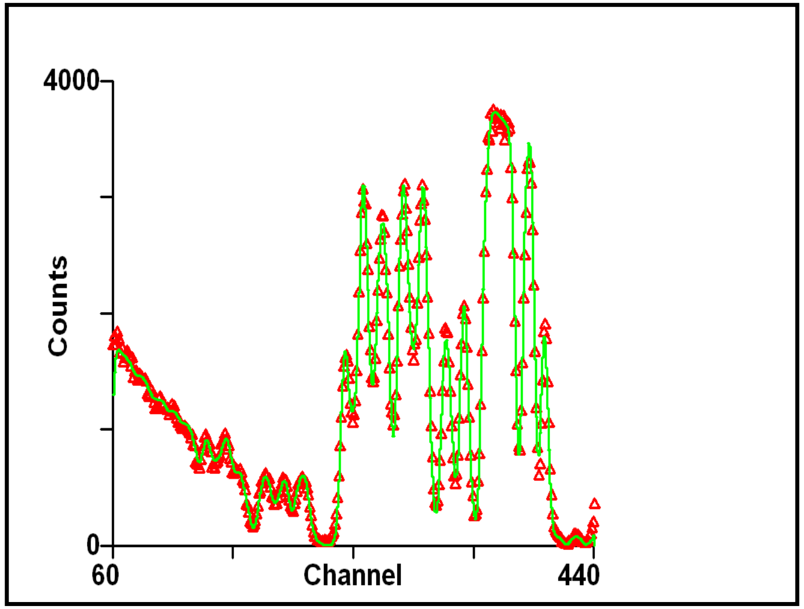




- Energy of ions scattering from nuclear collisions depends on mass and depth
- Detection limit around 0.1%

- Depth profiling with depth resolution <20nm
- Analytical cross-section σ (Coulomb potential)
- Single scattering (cf electron backscatters in SEM)

σ proportional to Z^2/E^2



- **Coulomb potential (accurate)**
- **Perfect fitting of complex structures (inverse problem solved)**

Spectrum of zirconia/silica multilayer optical coating (red), with DataFurnace fit (green)

RBS

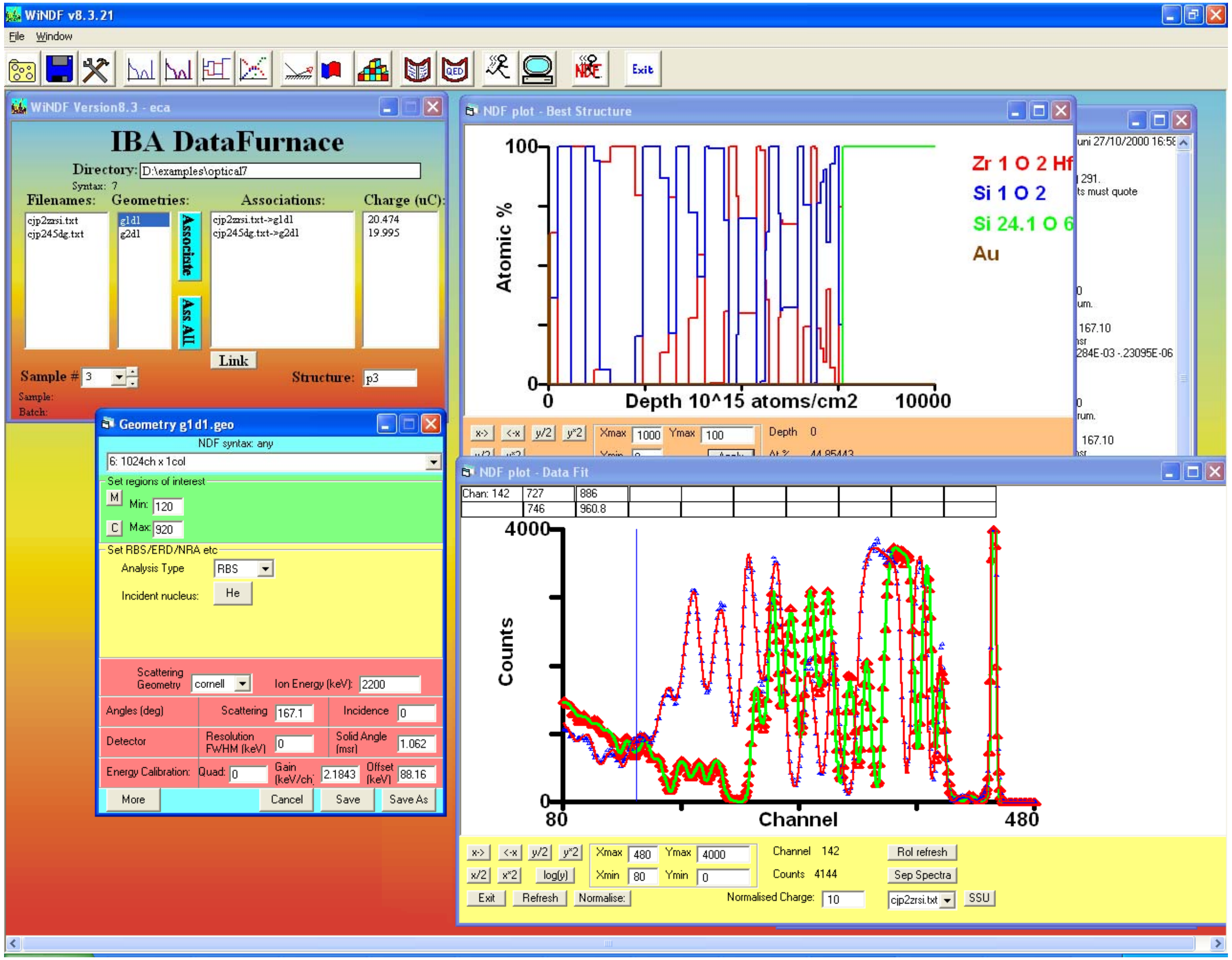
C.Jeynes++ Surface & Interface Analysis 30 (2000) 237-242

Molecules *contra* Ambiguity

2 angles 0^0 & 45^0

2 molecules

(glass substrate)



Directory: D:\examples\optical7

Syntax: 7

Filenames:	Geometries:	Associations:	Charge (uC):
cjp2zrsi.txt	g1d1	cjp2zrsi.txt->g1d1	20.474
cjp245dg.txt	g2d1	cjp245dg.txt->g2d1	19.995

Sample # 3

Structure: p3

Sample:

Batch:

NDF syntax: any

6: 1024ch x 1col

Set regions of interest

Min: 120

Max: 920

Set RBS/ERD/NRA etc

Analysis Type: RBS

Incident nucleus: He

Scattering Geometry: cornell

Ion Energy (keV): 2200

Angles (deg): Scattering 167.1; Incidence 0

Detector: Resolution FWHM (keV) 0; Solid Angle (msr) 1.062

Energy Calibration: Quad: 0; Gain (keV/ch) 2.1843; Offset (keV) 88.16

Xmax 1000 Ymax 100

Depth 0

Chan: 142	727	886
	746	960.8

Xmax 480 Ymax 4000

Xmin 80 Ymin 0

Channel 142

Counts 4144

Normalised Charge: 10

cjp2zrsi.txt

C.Jeynes++ Surface & Interface Analysis 30 (2000) 237-242

Molecules

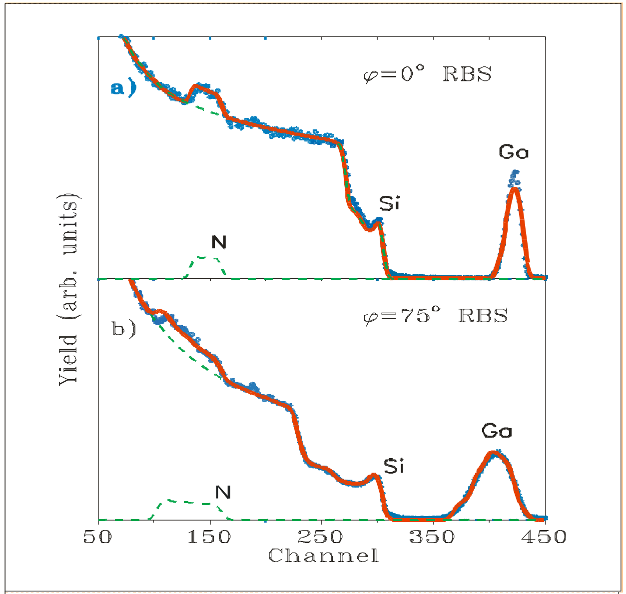
Five reasons for using molecules (***Occam's Razor***):

- Reduce number of free parameters
  - state space dimensionality increases with number of elements
- Better to constrain invisible elements with chemical priors
- Correlate direct signals for light & heavy elements
  - low sensitivity to light elements
- Allows other "complex" priors to be applied consistently
  - eg: "glass substrate"
  - eg: "silicide only near surface"
- Orthogonalise the problem
  - eg: determine substrate composition first

Wiiliam of Occam
(c1285-1347?)

Multiple Techniques

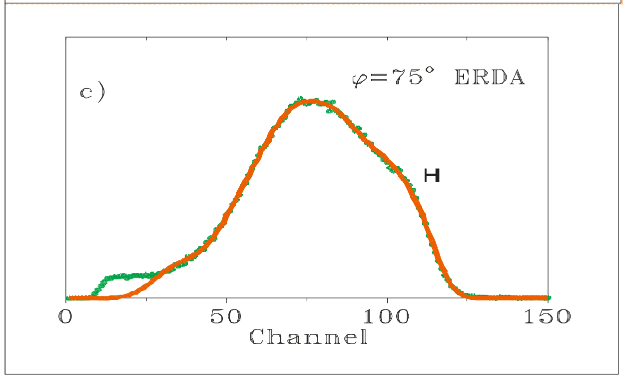
Elastic Recoil Detection



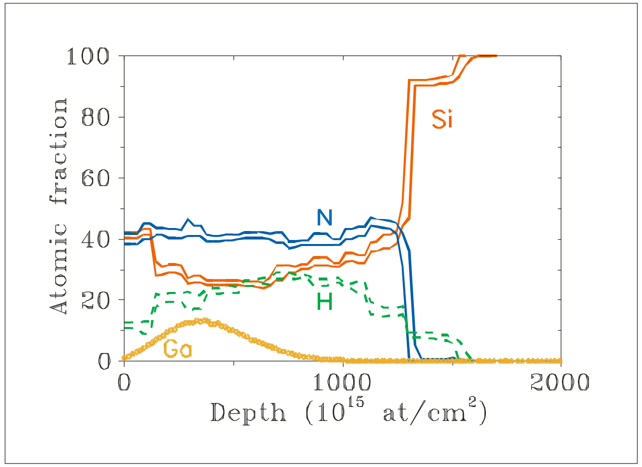
1.5MeV ^{4}He RBS

Normal incidence

Glancing incidence simultaneous with:



ERD



SiN$_x$:H on Si

Ga implant to form a-GaN$_x$?

Barradas *et al*, NIM B148, 1999, 463

Depth profile with uncertainties

Using Bayesian Inference

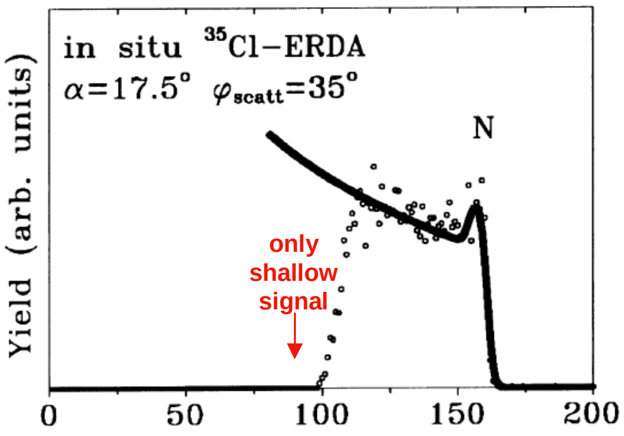
Jeynes *et al* J.Phys.D 36, 2003, R97

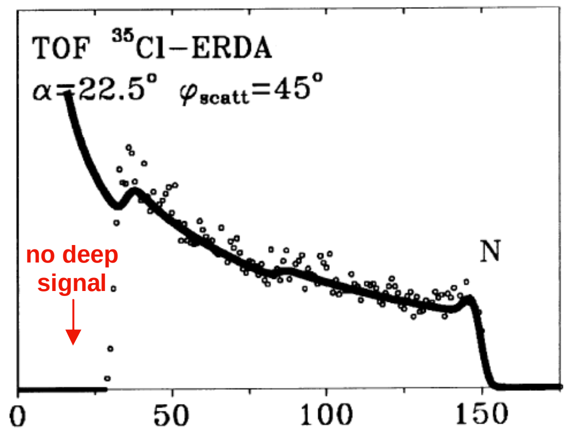
ERD

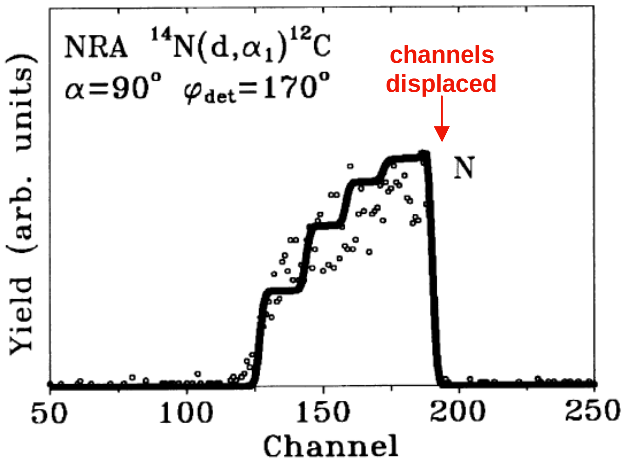
Multiple Techniques

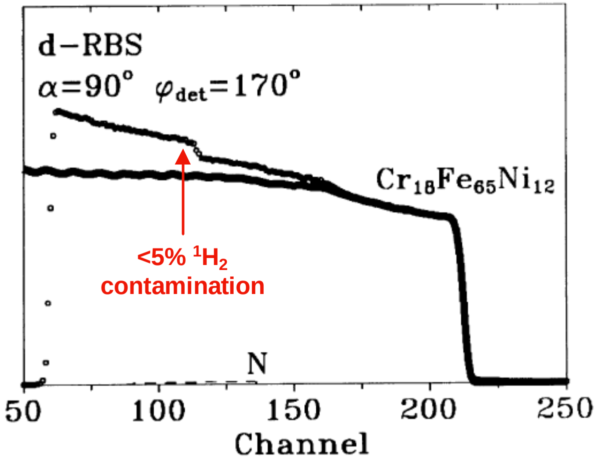
RBS/NRA/HI-ERD

N.P.Barradas, S.Parascandola, B.J.Sealy, R.Grötzschel, U.Kreissig, *Simultaneous and consistent analysis of NRA, RBS and ERDA data with the IBA DataFurnace*, NIM B161–163, 2000, 308–13









Austenitic stainless steel

(AISI 321, $Cr_{18}Fe_{65}Ni_{12}$) nitrided 4 h at 380°C by plasma immersion ion implantation (PIII).

35 MeV ^{35}Cl ERD:

angular resolved ionisation chamber 280mm 38mb isobutane "*in situ*" plus 1.5μm mylar range foil, 330keV

TOF: 60nm C foil for start, 284keV

1.4MeV d-RBS:

detector resolution 17keV

1.4MeV ^{14}N(d,α_1)^{12}C NRA:

Q=9.146MeV, 17keV

in situ ERD: high resolution

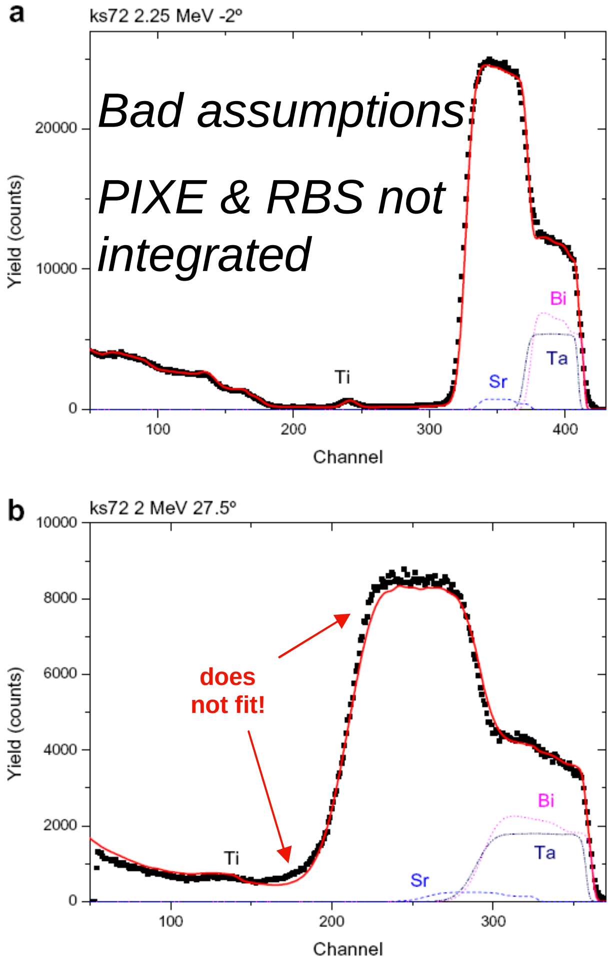
ToF-ERD: looks deeper

NRA: sees *all* the N

RBS: sees the metals

Multiple Techniques
RBS/PIXE

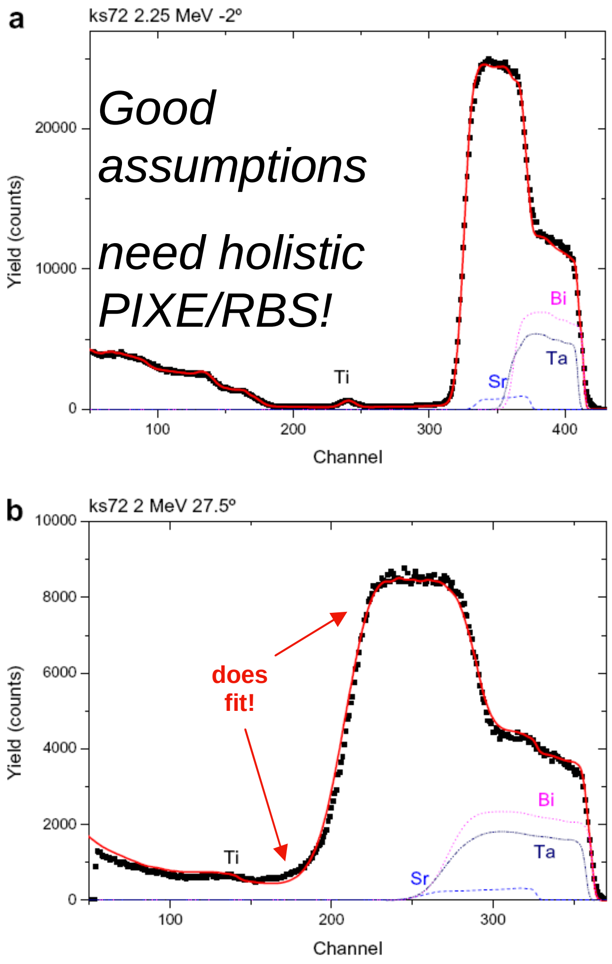
M.A. Reis, N.P. Barradas, C. Pascual-Izarra, P.C. Chaves, A.R. Ramos, E. Alves, G. González-Aguilar, M.E.V. Costa, I.M. Miranda Salvado, ***Holistic RBS–PIXE data reanalysis of SBT thin film samples*****, NIM B261. 2007, 439–442**



Bad assumptions

PIXE & RBS not integrated

does not fit!



Good assumptions

need holistic PIXE/RBS!

does fit!

SBT=$SrBi_2Ta_2O_9$:

- bismuth layered perovskite
- interesting ferroelectric
- spin coated thin films on $Si/SiO_2/Ti/Pt$ substrates

grazing incidence XRD:

- confirms perovskite structure with no second phases

PIXE line areas from AXIL

Details of the process (seeding, non-stoichiometry, interface diffusion, impurities) can be explored in detail with self-consistent PIXE/RBS

Occam's Razor!

Summary

- IBA data can be highly ambiguous
- Reduce ambiguity by using:
    - Multiple detectors (simultaneous data collection)
    - Multiple geometries (simultaneous or sequential data collection)
    - Multiple beams (sequential data collection)
    - Multiple techniques (simultaneous or sequential data collection)
- Strictly control prior assumptions with Occam’s Razor
    - Molecules (chemical priors)
    - Number and position of layers (physical priors)
    - Interface assumptions (roughness, diffusion etc)
- Explicitly and carefully determine all experimental parameters (!!)
- Write up properly (!!)