

Minerals laboratory staff develops new ICP-MS preparation method

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AGSO's Minerals Division laboratory staff has developed a new method of sample preparation for ICP-MS analysis that replaces the time-consuming, multi-step acid dissolution technique used to date.

The new method involves digesting pieces of the lithium tetraborate/lithium metaborate fusions that have been prepared and run for XRF major element analysis.

To date sample preparation for ICP-MS analysis at AGSO has been based on a method outlined by Jenner et al.¹ The method involves a series of acid digestion and drying stages over a period of four days. Comparisons between XRF Zr results and Zr results from the ICP-MS indicated that for many samples the method was not achieving total digestion of the zircon present. Subsequent replicates of problem samples also showed large variations in Zr results. Hot or cold spots on the hotplate surfaces, affecting digestion, may have been the reason for these variations.

Comparison of XRF and ICP-MS Cr results for those samples with significant Cr values suggests that similar problems are present for the dissolution of the refractory mineral chromite. Other elements present in refractory minerals generally tend to be at levels approaching or below the detection limit of the XRF method making comparisons meaningless.

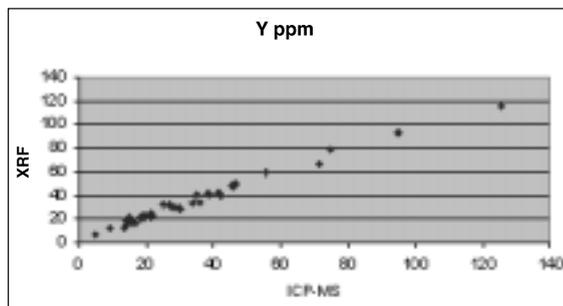
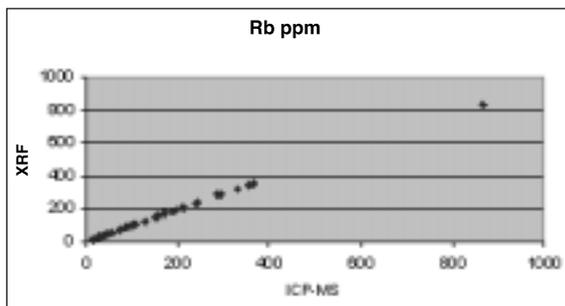
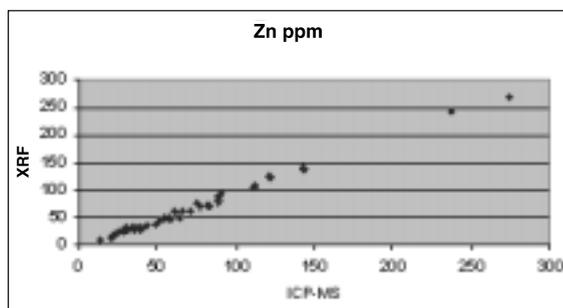
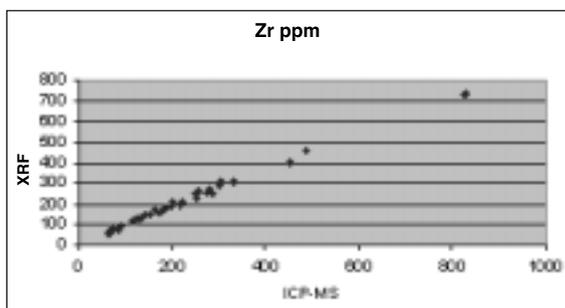
To overcome these problems laboratory staff first experimented with Parr bomb and microwave digestions. Little or no improvement was found with the microwave and only slight improvement with the Parr bombs. Steve Eggins from the Australian National University's School of Geology was using laser ablation on XRF fusions to do trace element analyses. His work led Minerals laboratory staff to the idea of digesting pieces of XRF fusions. Digesting the fusions proved straightforward.

The only problems encountered arose from contamination of the digest by the platinum ware used to produce the fusions. All platinum crucibles contained some rhodium and palladium, even the recently purchased 95% Pt/

5% Au crucibles. Rhodium is the most commonly used internal standard used in ICP-MS because of its position in the mass range.

Introducing it into the sample obviously precluded its use as an internal standard. Fortunately the elements for which Rh had been used as an internal standard were successfully divided between Ni 61 and Sm 147. Lanthanum was also present in many older crucibles—most probably residual from the Norrish and Hutton flux that the laboratory had used for many years. The La was removed successfully with a number of dummy fusions. One crucible that was highly contaminated with zinc is no longer used.

During the development of this method, the cause of an intermittent Ba and Pb contamination problem with the ICP-MS analysis was identified. One of a number of glass pipettes that could be used in the preparation of the internal standard was having these elements leached out of the glass by the 1% HF used in the preparation. No glassware is used in the ICP-MS laboratory now.



Method

Approximately 100 micrograms of chips from the smashed discs are weighed accurately into Savillex teflon vessels. Five millilitres of internal standard, one millilitre of HF and five millilitres of HNO₃ are then added.

The vessels are sealed and heated for 12 hours overnight at 120 degrees centigrade on a timed hotplate, such that cooled samples are ready the following morning. The digests are then transferred to volumetric flasks and made up to volume ready for the ICP-MS.

Occupational health and safety

There are substantial benefits from an occupational health and safety perspective. The digests take place in a sealed vessel. If the fume cupboard system failed, dangerous acid fumes would not leak (unlike the present situation). The use of acids, particularly HF, is substantially reduced. With this method one millilitre of HF is used instead of six, and five millilitres of HNO₃ are used instead of 18. This greatly reduces staff handling of acids, with less acid needing to be distilled and stored in the laboratory.

Table 1. Zr results obtained on some international standards

Standard	ICP-MS Old	ICP-MS New	AGSO XRF	Recommended value ^e
W-2	78 ppm	95 ppm	93 ppm	94 ppm
BIR-1	15	15	15	15.5
DNC-1	36	37	36	41
QLO-1	171	189	188	185
BHVO-1	151	176	175	179
AGV-1	205	235	235	227

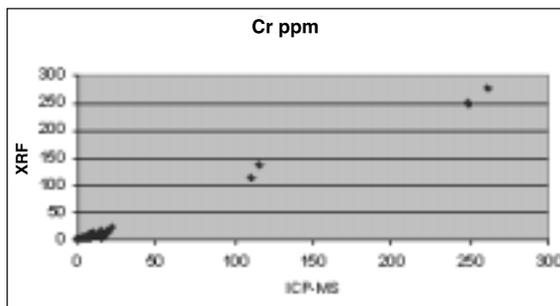
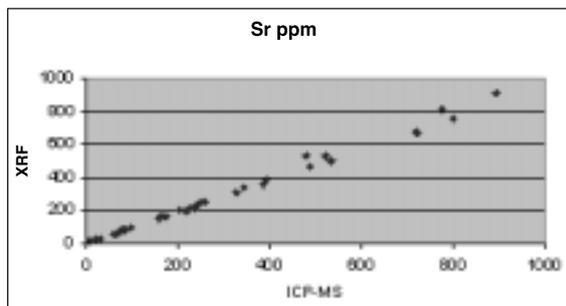
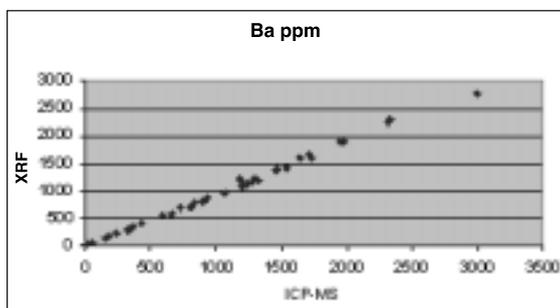
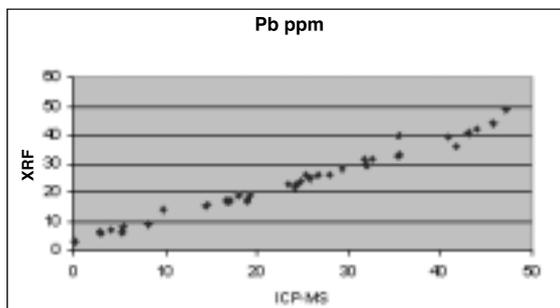
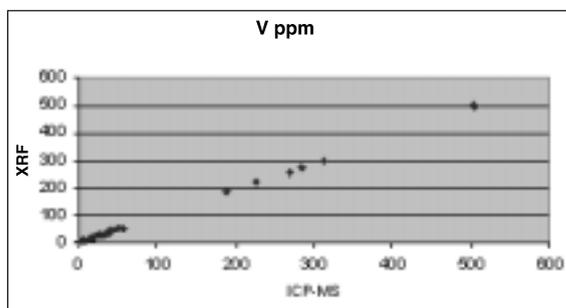
Sample digestion

The sample is totally digested. Any undissolved sample in the glass disc creates stress points and the disc shatters. Because the discs have survived XRF analysis and a few days stored in a plastic bag, laboratory staff can be confident that dissolution in the glass is complete.

Disregarding the fusion process, which is standard practice for the XRF, this method is a one-step 24-hour preparation compared to a multi-step four-day procedure. The time could be cut even further by using a microwave for small lots of 'specials'.

Contamination of samples should be effectively eliminated since the digestion takes place in a sealed container. There are no drying stages as in the current method where samples spend many hours in open vessels. Because the sample is totally in solution, laboratory staff can now confidently analyse for those elements associated with the refractory minerals—elements such as Zr (see table 1), Hf, Cr and the REE likely to be tied up in zircons.

Figures 1–9. XRF vs ICP-MS: Result comparisons for a number of elements from a recent suite of samples



The distribution of zircon, if present, in a powdered sample is an excellent indicator of sample homogeneity. Any major discrepancy in Zr results from the XRF and the ICP-MS will now suggest problems with the sample grinding rather than analytical problems. Results, particularly trace results, could be then treated with appropriate caution or the sample(s) reground and reanalysed.

The laboratory will be able to report both results for those elements that can now be equally well determined by XRF and ICP-MS. These elements will probably be Ba, V, Cr, Ni, Cu, Zn, Rb, Sr, Y, Zr and Pb because they are generally present in silicates at levels significantly above the detection limit of the less-sensitive XRF (see figures 1 to 9).

Although the effective sample weight in the final solution is smaller than presently used, the weight used to make the fused disc is approximately three times larger than at present. The end result is that laboratory staff is now using what should be a more representative aliquot of the sample.

Because discrete chips of glass are used, there are no problems with electrostatic charges that cause segregation in some sample powders. One chip digests as easily as a dozen smaller pieces.

Similar rock standards will routinely be run with each batch of both XRF and ICP-MS. Collection and storage of this data will continually monitor the performance of both techniques.

Disadvantage

Lithium and boron analyses will no longer be available from the Minerals Division laboratory because of the Li and B present in the flux and their memory effect within the spectrometer.

References

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2. Govindaraju K, ed. 1994. *Geostandards Newsletter*, special issue Jul; 18.

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Bonaparte Basin

Geochemical characteristics of hydrocarbon families and petroleum systems

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The Bonaparte Basin has been actively explored for more than 20 years, with oil production from several fields (Jabiru, Challis-Cassini, Laminaria-Corallina, Elang and the depleted Skua field) and proposed production from giant gas/condensate fields (Bayu-Undan, Sunrise-Loxton, Shoals-Troubadour and Petrel-Tern). Despite this focused exploration and appraisal, to date geoscientists have had a relatively poor understanding of the region's petroleum systems.

To improve this understanding, isotopic and biomarker analyses of numerous oils, condensates and gases have been undertaken to geochemically characterise the hydrocarbon families in the Bonaparte Basin, and to correlate them with likely source rocks. Preliminary results of this study show that two Palaeozoic and seven Mesozoic oil families can be identified in the Bonaparte Basin. Details of the petroleum system active in this basin were presented at the recent AAPG International Conference in Bali (October 15–18, 2000) by Dianne Edwards and John Kennard, and continue to be investigated by AGSO's North-north-west Regional Project.

The Bonaparte Basin lies between north-western Australia and the island of Timor (figure 1). It has a complex tectonic history involving two phases of Palaeozoic extension and Late Triassic compression prior to the onset of Mesozoic extension.

Initial rifting occurred in the Late Devonian to form the north-west-trending Petrel Sub-basin in the south-east. The resultant thick Late Devonian–Carboniferous rift and sag succession was orthogonally overprinted in the Late Carboniferous to Early Permian by north-east-trending rift basins to form a proto-Malita and possible proto-Vulcan Sub-basin. Late Jurassic extension resulted in a series of linked, north-west-trending (Vulcan Sub-basin and Malita Graben) and south-east-trending (Sahul and Flamingo Synclines) intracontinental grabens. Thick marine mudstones accumulated within these grabens, and passed laterally to fan delta sandstones on the adjacent horst blocks and terraces. These Mesozoic depocentres are surrounded by structural highs (Ashmore Platform, Londonderry High, Sahul Platform and Darwin Shelf; figure 1) which have relatively thin Jurassic–Cretaceous sediments across an uplifted and eroded Triassic–Palaeozoic section.

Most of the commercial and soon to be developed oil and gas accumulations are reservoirised in Middle and Upper Jurassic sandstones (Plover and Montara/Elang Formation, respectively; figure 2). Commercial accumulations also occur in Upper Triassic and Upper Cretaceous sands in the Vulcan Sub-basin. In the Petrel Sub-basin, gas and gas/condensate accumulations occur in the Upper Permian Hyland Bay Formation (Petrel and Tern Fields, Fishburn-1 and Penguin-1), and gas discoveries on the Londonderry High (Prometheus-1, Ascalon-1A) and Sahul Platform (Kelp Deep-1) also occur within this unit (figure 2).

Hydrocarbon families

Oil–oil comparisons were made using cluster and principal component analysis—the results of which are displayed as a dendrogram in figure 3. The GeoMark protocol was adhered to which utilises 16 geochemical parameters (two bulk carbon isotopic values, 13 source-specific terpane