Fig 3.1

ERA **Energy Resources of Australia Ltd - Ranger Mine**
ACN 008 550 865

Jabiru Environmental Laboratory: ph: (08)89381331
fax: (08)89381302
Chemistry Laboratory: ph: (08)89381325
email: geoffrey.kyle@north.com.au

MEMORANDUM

TO : Andrew Jackson
FROM : Geoffrey Kyle
SUBJECT : TECHNICAL MATTERS
DATE : 16/2/98
REF : gjk:gjk:16feb98a.lwp

Andrew,

Please find attached a statement detailing some of the technical matters which were identified during the course of my discussion with Ian Shakespeare.

As suggested by Ian, I have restricted the exercise to a presentation of the verifiable facts.

Regards,

Geoffrey Kyle.

Sydney Office Level 18, Gateway, 1 Macquarie Place, Sydney NSW 2000 Australia Tel: (02) 9256 8900 Fax: (02) 9251 1817
Ranger Mine Locked Bag 1, Jabiru NT 0886 Australia Tel: (08) 8938 1211 Fax: (08) 8938 1203

A Member of the NORTH Group

Fig. 3·1·1

- Balance

The analytical balance was declined a NATA certificate for four-place operation on 16/8/96. On 26/10/96 the balance was labelled as suitable only for unrounded three-place readings. For two months until then, all analyses requiring the balance continued to record and use the fourth place.

The balance failed a required in-house calibration check on 24/9/96, and was later internally tested against three place criteria on 22/10/96 and 25/3/97 and passed.

Up until the balance was replaced in 10/97, the fourth place continued to be employed for routine and statutory work, and some early work on the Jabiluka project, (excluding radium).

Other volumetric instruments whose Australian Standard calibrations depend on the four place accuracy of the balance failed required in-house performance checks but were deemed to pass when compared with three place criteria, (eg. Gilson Dilutor, 29/1/97).

A fully-functional analytical balance is a critical item of equipment. Its performance is either specified or implied in most of the methods employed at this laboratory, including those with NATA registration. The production of all primary, intermediate and working standards must be traceable through an appropriately certified analytical balance.

Failure to replace the balance immediately had the potential to compromise results, (see Radium below), and in some methods represented non-compliance with the requirements of NATA registration, (preparation of standards, calibration compliance checking, and quantitative dilution of samples). In the case of Total Suspended Solids, where a three place balance is not capable of reporting less than 10 mg/L, such results were reported and passed through the quality system.

Fig. 3.1.2

- Radium

After QTC reported that the balance would not support four place measurements, statutory radium analyses continued to utilise the fourth place for more than two months until 10/96 when the balance was labelled as described above. Thereafter, the barium tracer material was diluted by a factor of ten, and ten times the original mass was weighed out and recorded on the local work sheet to three decimal places.

No test work was performed to determine the effect of dilution and validate the change of procedure. The written method and electronic calculation were not altered, and data were entered into the electronic calculation after moving the decimal place in the recorded mass one place to the left such that the report hard copy recorded the mass of ~ 0.2000 g. instead of the actual mass weighed, which was ~ 2.000 g.

The revised process encountered difficulties when a large number of sequential results were observed to vary consistently from historical trends. The discrepancies were attributed to a putative tenfold dilution error in the preparation of the diluted barium standard. The results were corrected by dividing the mass of the erroneously diluted standard by a factor of ten and then recalculating.

Radium analyses were also compromised by reducing the gamma count time from 600 to 300 seconds. Even though the majority of the samples submitted for radium analysis will report at very low levels, no test work was done to determine the effect of halving the statistical population of the recorded count data. The analyses proceeded for some time using standards which had been prepared and verified at the specified 600 seconds. The standard counts were scaled to approximate the sample count time. More appropriate standards are now in use, but the 300 second count time is routine.

Radium analysis is a skilled task. Experience with gravimetric techniques is required for the classical wet end, and reliable instrumentation which is supported by adequate statistical data is necessary for the alpha and gamma counting procedures which yield the quantitative data.

This very important statutory and EIS parameter is currently analysed by an inexperienced person using a semi-quantitative, three place top pan balance, whose certified limit of performance is +/- 0.021 g. This top pan unit is used without its shroud and lid, accessories which are necessary to achieve the limit of performance quoted. This level of accuracy in the determined mass of the tracer material is transposed into the electronic calculation in the form of 0.2 g. to four decimal places. These changes have not been tested except by reference to the internal "recovery" calculation, which is itself dependent on the same data.

Fig.3.1.3

- Alkalinity

The method for alkalinity, P/N 1106, was originally written and registered for use with a particular model auto-titrator and reported in units of calcium carbonate. It was reviewed and rewritten by its author to reflect the 1992 change of reporting units to carbonate and bicarbonate. The resultant changes were documented and accounted for in the new machine factors. The method was subsequently modified to suit a new model titrator. This involved no factor or programme change.

The method was subsequently modified again to address a requirement to document intermediate calculations for each determination, and to clarify a change to the data entry procedure for the LIMS system which received the results electronically.

As part of a method review, which followed the NATA review delegation finding that some laboratory documentation was not up to standard, many of the RUM methods were rewritten to the relevant Australian Standard, including Alkalinity. The revision was checked and approved and went into service. The method was later included in a general NATA review and passed.

The method was later further reviewed and a resultant rewrite was checked and approved. It went into service around 9/97.

This latest version of the method appears to contain errors in respect of the internal quality control standard and the calculation units of results produced from Methods 3 and 4. The errors apply only to the internal quality control standard, and to rare samples having a pH in excess of 8.3.

The routine external quality control standard reports within the range specified for low level alkalinities, according to Method 5, and Methods 1 and 2, which account for the vast majority of samples, were not involved, being unchanged from the earliest version.

The text of the method dealing with the preparation of an internal reference material standard, (4.4.8), contains an apparent error, (hydrolysis and speciation of primary salt not accounted for), which predicts an incorrect value for the quality control standard as it is to be determined empirically according to Sections 6.1 and 6.2.

0.164 g. sodium carbonate = 175 mg. calcium carbonate (4.4.8) (~ 189 mg. bicarbonate)

For example: actual print-out data from an analysis of an aliquot of that standard, whose pH was around 10.4, was: R = 83.317 mg/L and R2 = 111.53 mg/L. According to the method, both are expressed as calcium carbonate. From the method,

P = R / 2 = 41.66 mg/L and M = R2 = 111.53 mg/L. Thus T = P + M = 153.19 mg/L as calcium carbonate, (6.2).

Since $P < T / 2$, “carbonate alkalinity” will be reported as 2P or 83.32 mg/L, and “bicarbonate alkalinity” as $(T - 2P)$ or 69.87 mg/L, both as calcium carbonate. (App. 4). Since the unit of reporting is no longer calcium carbonate, these must then be converted to **49.95** mg/L as carbonate and **85.17** mg/L as bicarbonate for the “carbonate” and “bicarbonate” alkalinities respectively.

If the same data are used to calculate a result based on the machine-resident constants in the auto-titrator, and the theory of speciation, the following is obtained:

$R = 83.317$ mg/L as carbonate, and $R2 = 111.53$ mg/L as bicarbonate. From theory;

$P = R / 2 = 41.66$ mg/L as carbonate, (69.49 as calcium carbonate), and
$M = R2 = 111.53$ mg/L as bicarbonate, (91.49 as calcium carbonate). Thus
$T = P + M = 160.98$ mg/L as calcium carbonate, (6.2).

Since $P < T / 2$, “carbonate alkalinity” will be reported as 2P or **83.32** mg/L as carbonate, and “bicarbonate alkalinity” as $(T - 2P)$, (22.01 mg/L as calcium carbonate), or **26.83** mg/L as bicarbonate.

The same data calculated by the formula provided in the text of the original method yields “carbonate alkalinity” of **83.32** mg/L as carbonate, and “bicarbonate alkalinity” as **28.21** mg/L as bicarbonate. (The text of that method acknowledges rounding constants to integers for calculation of “bicarbonate” alkalinity directly as $(R2 - R)$ as bicarbonate.)

If another method is used to determine the total stoichiometric alkalinity to pH 4.5 of that standard, say, using Method 2, reported as bicarbonate, the results agree with the theoretical prediction.

The original machine-resident constants remained active throughout the several reviews of the written method and all sample results reported by Methods 1,2 and 5 of this procedure are sound. Nevertheless, an internal quality control error was instituted, approved and perpetuated for some time without being exposed by the quality system.

Fig.3·1·4

- ICP Performance and Detection Limits

No documentation seems to exist which supports QC and performance criteria quoted in respect of ICPOES analyses. Beyond a statement of limits for some analytes given in the text of the 12/92 edition of the laboratory method, (see below), and a page in the maintenance log from 11/90 which consists of a computer print-out software summary of background equivalent concentration and detection limits for 14 analytes at 21 wavelengths, (obtained from the analysis of blank and synthetic solutions under unspecified conditions, and calculated by an unknown software algorithm.), no data which address the verification of performance are extant.

There should be two sets of data, one for each of the matrix types analysed. (That is, filtrate and reside. Acid-extractables were not analysed until around 1994.) According to the relevant authorities, the sets should have been appended to the registered method and verified empirically as a regular, documented QC exercise. A minimum regime would have produced data sets on commissioning and NATA registration, and thereafter annually, and after major component changes.

The instrument concerned generates a great deal of baseline and low-level data whose credibility is predicated, at least in part, on the presumption of documented performance characteristics, including detection limits. For most of its service life it has not been subject to a programme of routine performance checking against established standards.

During a period of exception to that, and when the instrument was performing well, several sets of empirical data were produced according to the recommendations of the testing authority and reported through the laboratory quality system. Some of those data supported the values routinely quoted and some did not.

For the currently relevant suites; for filtrates, K, Fe, Cu and particularly Al were detected above the quoted limits, and Na, Mg, Ca, SO4, Mn and Zn either met or bettered their respective quoted limits. For residues, only Mn met its quoted limit. (See table below.)

The detection limits currently quoted are the originals, used since the ICP method first addressed them in 1992, and possibly since the instrument was commissioned in 1989. During its life, the ICP has occasionally suffered serious maintenance problems and had several major components either changed out or repaired. It operates in an environment of somewhat variable conditions and is driven by persons of varying technique. It has never been the subject of regular professional service. Quoted performance characteristics therefore must depend to a significant extent on consistent application of consistent conditions to an appropriate standard method.

At various times, significant and undocumented changes have been made to some or all of those factors in the course of routine operation. Modifications to instrumental operating conditions have been made without subsequent verification of performance criteria and detection limits, and without reference to the quality system.

All ICP analyses described in P/N 1119, are performed by the same parent method. Single calibrations are used to quantify samples whose undiluted concentrations vary from below detection limits to the calibration maxima of 20 ppm for "cations" and 1000 ppb for metals. Process samples whose concentrations can be 2 orders of magnitude outside the calibration maximum are analysed, after appropriate dilution, by the same method as statutory samples of baseline level.

Identical parameter values apply for all instrument functions and plasma conditions. The software capabilities for individual background correction and spectral compensation are not utilised. Internal quality control standards of a concentration 20 to 50 percent of the calibration curves, are run within batches. An external standard, whose concentration is 10 percent of the curve, is checked in singlicate on a monthly basis. All tolerances are set at the nominal plus or minus 5 percent. Empirical verification of the stated analyte concentrations of successive batches of both internal and external standards applies a plus or minus 5 percent nominal tolerance to a single data set of five elements which is acquired in a single run. In recent times, a quarterly calibration interval has been observed.

DETECTION LIMITS

ANALYTE		INITIAL (stated in 10.2, method, rev.1)	CURRENT (routine use since 1992)	EMPIRICAL CHECK (November, 1996)		
				(F)	(R)	(AExt)
Na	ppb	5	100	100	n/a	n/a
K	ppb	50	100	200	n/a	n/a
Mg	ppb	1	100	100	n/a	n/a
Ca	ppb	1	100	100	n/a	n/a
SO4	ppb	100	100	100	n/a	n/a
Mn	ppb	1	1	1	1	1
Cu	ppb	2	2	3	4	3
Zn	ppb	2	2	1	4	2
Fe	ppb	n/g	2	3	3	2
Al	ppb	n/g	10	20	15	18
Pb	ppb	20	n/u	20	20	20
U	ppb	70	n/u	130	110	100
PO4	ppb	100	n/u	n/t	n/a	n/a

n/a = not applicable, n/g = not given, n/t = not tested, n/u = not used

At various times the instrument and method have seen extensive duty analysing commercial environmental and geochemical samples from a diverse range of sites. Elements analysed included: Ni, Co, Cr, Cd, As, Se, Sb, Si, V, Mo and Tl. These analytes were calibrated from cocktail solutions in concentrations of up to 10,000 ppb each, and which included the routine Ranger suite of analytes at up to 1,000 ppb each, (for metals.) No test work is available to document the performance of the instrument and its single method under those conditions. Those elements are no longer quantifieded. The calibration solutions were rationalised when the method was rewritten to Australian Standard in 11/96, and have since contained only those analytes relevant to the current operational requirements of the method. That is, those tested in 11/96 less Pb and U.

Fig. 3.1.5

- Zn/DIW Investigation

There is a history of puzzling inconsistencies in zinc results. The incidence is recurrent and apparently episodic. It has variously been attributed to contaminated acid dispensettes, contamination of samples during filtration in the clean room, and contamination emanating from commercial acids which had not been screened.

One investigation examined a great deal of historical digestion and filtrate data and indicated a possible contamination problem in the DIW system. Further sampling and testing of DIW from various sources confirmed that a contamination was likely and narrowed it to a brass tap fitting in the digestion fume hood. Other fittings on the DIW ring main, including several of the taps, were found to be brass.

A report in 7/96 detailed the results and recommended that the DIW system be refitted with plastic components. To that was added a recommendation that method development work would be required to eliminate the possibility that measurement errors close to detection limit were contributing to, or masking, the apparent problem. The measurement of zinc was at that time compromised by the use of multi-elemental cocktails for bulk calibrations. (Refer to comments on methodology in the discussion of performance and method detection limits for the ICPOES instrumentation.)

A work request was raised and brochures describing appropriate fittings for the DIW system were sent to a contractor. That work requested has not been performed. The calibration matrix has been rationalised to a suite appropriate to the current statutory requirements. The ICP method continues to rely on a single set of conditions. Only ultra-pure acids are now used, and DIW is not drawn from the suspected outlet.

Another investigation of the zinc/DIW problem was later instigated after further problems with the low level analysis of zinc. The results of that investigation are apparently undocumented and no test data or notes are extant.

Recently another investigation of the problem was requested. No action has been taken on the recommendations of previous investigations. Zinc analyses are subject to blank correction at the discretion of the analyst. Such corrections vary between 2 and 9 ppb and have been as high as 12 ppb. Results are reported subject to a detection limit of 2 ug/L.

Fig 3-2

P.O. Box 561,
Jabiru, N.T., 0886.

November 11 th., 1998.

The Manager,
Department of Environment, Safety and Health,
Ranger Uranium Mine,
Locked Bag 1,
Jabiru, N.T., 0886.

Andrew,

As you will be aware, I have resigned from my position as a Technical Officer in the Chemistry Section of the RUM Environment Laboratory. Separation will be effective from December 11 th., 1998.

I would like to take this opportunity to remind you of your commitment to provide me with a document which states the results of David Jones' adjudication of the five technical matters which I raised during the course of my "conflict resolution" sessions with Allan Ryan.

Not withstanding my intended departure, the "further clarification" of those technical matters, as it is described in the mediation report, remains an important professional issue with me.

Yours sincerely,

Geoffrey Kyle,
MRACI CChem.

Fig. 3.3

ERA Energy Resources of Australia Ltd – Ranger Mine
ACN 008 550 865

MEMORANDUM

TO : Geoffrey Kyle
FROM : Andrew Jackson
SUBJECT : **Technical Matters**
DATE : 03 December 1998
REF :

Dear Geoff,

My apologies for the delay in my response to your e-mail of 11 November 1998, but I have been diverted onto other matters entirely for the last few weeks.

Having discussed these issues at the feedback meeting held with Ian Shakespeare, I understood that it had been agreed that these matters were in the past, and further I have no record of (nor believe there was) a commitment to provide " a document which states the results of David Jones adjudication of the five technical matters ".

Despite that, I provide the following advice in relation to the issues you raised viz;

- analytical balance
- radium
- alkalinity
- ICP performance and detection limits
- Zn/DIW investigation

David Jones agreed that each of your points has technical merit. Sometimes, however, pragmatic decisions are required and, as a result, the system may not be perfect at all times. This does not mean, however, that the overall perfomance is, or was, compromised.

You will note however, that over the past 8 months the capital acquisition process has been followed in a prioritised manner and the issues you raised have been substantially addressed – in particular the issues of the balance and water supply. In other cases procedures have been reviewed.

I am satisfied that ERA's laboratory strives to operate to a very high standard and am proud of the work done by everyone associated with it.

Good luck in your future endeavors.

Yours sincerely

Andrew Jackson
Manager, Environment, Safety & Health

Sydney Office Level 18, Gateway, 1 Macquarie Place, Sydney NSW 2000 Australia Tel: (02) 9256 8900 Fax: (02) 9251 1817
Ranger Mine Locked Bag 1, Jabiru NT 0886 Australia Tel: (08) 8938 1211 Fax: (08) 8938 1203
A Member of the [illegible] Group