

CERTIFICATION REPORT

ACIRS-A1-2016

Fly Ash Reference Material

Date of Issue:	June, 2016
Valid to:	June, 2026
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1. Introduction

This report describes the preparation and certification of ACIRS–A1-2016 which comprises a sealed jar containing approximately 80 g of coal fly ash reference material at 63 µm nominal top size.

Production and certification was conducted in accordance with the technical and production requirements of ISO Guide 34 and the associated guidelines provided in ISO Guide 35 and overseen by ACIRS personnel representing Australian Coal Research Limited and the Australian Coal Preparation Society.

This sample is intended to be used for quality control purposes on similar ash samples.

2. Property Values

Values provided are on samples which have been pre-ignited (see clause 3) before analysis.

Table 1 Assigned Property Values (on pre-ignited samples)

	Property Value ¹	Standard Deviation ²	Standard Uncertainty ^{3a}	Expanded Uncertainty ^{3b}	Number of laboratories
Ash analysis properties					
SiO ₂ wt%	44.1	0.96	0.17	0.34	49
Al ₂ O ₃ wt%	28.9	0.58	0.11	0.22	45
Fe ₂ O ₃ wt%	14.6	0.34	0.07	0.14	39
CaO wt%	6.05	0.16	0.03	0.06	49
MgO wt%	1.25	0.05	0.01	0.02	47
Na ₂ O wt%	0.43	0.04	0.01	0.02	49
K ₂ O wt%	0.46	0.02	0.004	0.008	44
P ₂ O ₅ wt%	1.26	0.04	0.01	0.02	41
TiO ₂ wt%	1.56	0.05	0.01	0.02	47
Mn ₃ O ₄ wt%	0.22	0.02	0.004	0.008	31
BaO wt%	0.18	0.01	0.002	0.004	38
SrO wt%	0.16	0.01	0.002	0.004	42
SO ₃ wt%	0.32	0.04	0.01	0.02	40
Ash fusibility					
Reducing temperatures					
Deformation °C	1257	18	4	8	37
Spherical °C	1287	13	3	6	38
Hemispherical °C	1309	17	4	8	37
Flow °C	1367	34	7	14	38
Oxidising temperatures					
Deformation °C	1349	18	4	8	35
Spherical °C	1383	8	2	4	34
Hemispherical °C	1398	9	2	4	35
Flow °C	1429	17	4	8	35

Table 2 Indicative Values

	Indicative Value ⁴	Standard Deviation ²	Standard Uncertainty ^{3a}	Expanded Uncertainty ^{3b}	Number of laboratories
Chromium mg/kg	58	9	2	4	25
Cobalt mg/kg	43	6	2	4	22
Copper mg/kg	99	8	2	4	23
Lead mg/kg	47	6	1	2	22
Nickel mg/kg	47	6	1	2	27
Vanadium mg/kg	176	11	3	6	24
Zinc mg/kg	90	12	3	6	26

1. Property values are the best estimate of the true value for the measurand and are based on the robust mean of participant results from a CANSPEX proficiency testing program. Property values are provided where analysis of data provides an acceptable degree of uncertainty around the robust mean (mean of means) of participant results. The CANSPEX dataset includes results of multiple analysis methods and from in-house methods. Results were excluded which did not meet ACIRS precision criteria, or if the result reported by an in-house method was not within the normal distribution of standard national and international test methods. Biases between these methods, shown in Table 3, were not observed.
2. The standard deviation (s^*) is a robust value used to derive the likely range of results. The value for a measurand from a randomly chosen laboratory would be expected to lie within 2 standard deviations of the certified value with 95% probability.
3. Uncertainty provides the user with information on the likely range of the true (but unknown) value for each parameter and has been estimated in accordance with the Guide to the Expression of Uncertainty in Measurement (GUM)
 - a. Standard Uncertainty (u_a) is a robust value estimated at $1.25 \times s^*/\sqrt{n}$
 - b. Expanded Uncertainty (U) is calculated from $u_a \times$ a coverage factor $k = 2$ corresponding to a level of confidence of about 95%.
4. Indicative values are provided where the uncertainty of the robust mean is considered unacceptably high. This may be due to a poorer level of precision than expected or insufficient data. Indicative values should be used on a fitness for purpose basis.

3. Instructions for Use

This sample should be stored in a cool, dark place in original containers with the lid tightly sealed. Before sub-sampling the sample should be thoroughly mixed by end-over-end rotation. Immediately prior to weighing the sub-sample shall be pre-ignited to 815°C for 15 minutes, and cooled in a desiccator over freshly regenerated, self-indicating silica gel.

Note: The pre-ignition temperature is based on Australian Standard test procedures. Pre-ignition temperatures between 750°C and 815°C will not impact the characterised values of this sample.

Samples shall be handled in accordance with the Safety Data Sheet available from www.acirs.com.au/products/acirs-sulfur-reference-materials-/

4. Sample Source and Preparation

A bulk sub-sample of approximately 85 kg was taken from an Australian coal fired power station. The material was re-ignited at 815°C and then blended in a drum mixer for 6 hours. The bulk sample prepared in this way was then repeatedly mixed and divided by rotary sample division until samples of approximately 800g were obtained. These samples were reconstituted into 12 primary samples which were again repeatedly mixed and divided by

rotary sample division until representative samples were obtained of approximately 80 g each. This is the nominal maximum mass with the minimum mass of 70g.

5. Homogeneity testing

Homogeneity testing was conducted by an independent laboratory on 24 samples selected by stratified random sampling from the production lot. Homogeneity was assessed by analysis of SiO₂, Al₂O₃ and Fe₂O₃ by AS1038.14.3. Satisfactory sample homogeneity for this sample was established after evaluation in accordance with ISO Guide 35, 2006.

6. Characterisation

ACIRS-A1-2016 was analysed as an unknown sample in the proficiency testing program CANSPEX 2016-1 conducted by Quality Associates International Ltd.

Characterisation was conducted by ACIRS using robust statistical techniques in accordance with the guidelines of:

- IUPAC, 2006 International Harmonized Protocol for the Proficiency Testing of Analytical Chemical Laboratories
- ISO 13528, 2015, Statistical methods for use in proficiency testing by interlaboratory comparison, and
- ISO Guide 35,-2006, Reference Materials – General and statistical principles for certification.

NOTES:

- Assigned property values are based on the robust mean of the proficiency testing program dataset.
- The proficiency testing program dataset includes analyses conducted by nationally and internationally recognised test methods and in-house methods.
 - Data was excluded from the proficiency testing program dataset which did not meet ACIRS precision criteria. In-house methods were included when within the normal distribution of recognised national and international methods of analysis.
 - Where data from multiple methods have been combined, significant method biases were not detected.
 - Test methods used in the ACIRS characterisation are shown in Table 3.

7. Period of Validity

The stability of assigned property values will be monitored by ACIRS. It is the responsibility of the user to obtain the most recent Technical Report and Product Information Leaflet for this reference material available at www.acirs.com.au/

Table 3 Test methods

Parameter	Method	n	Parameter	Method	n	Parameter	Method	n
Ash Analysis Parameters								
SiO2	AS 1038.14.3	5	Na2O	AS 1038.14.3	5	BaO	AS 1038.14.3	5
	ASTM D3682	9		ASTM D3682	10		ASTM D4326	11
	ASTM D4326	15		ASTM D4326	14		ASTM D6349	17
	ASTM D6349	16		ASTM D6349	17		Other *	5
	Other *	4		Other *	3			
Al2O3	AS 1038.14.3	5	K2O	AS 1038.14.3	5	SrO	AS 1038.14.3	5
	ASTM D3682	6		ASTM D3682	9		ASTM D3682	4
	ASTM D4326	15		ASTM D4326	16		ASTM D4326	14
	ASTM D6349	15		ASTM D6349	13		ASTM D6349	17
	Other *	4		Other *	1		Other *	2
Fe2O3	AS 1038.14.3	5	P2O5	AS 1038.14.3	5	Mn3O4	ASTM D 6357	17
	ASTM D4326	13		ASTM D4326	15		AS1038.10.0	1
	ASTM D6349	17		ASTM D6349	16		Other stds**	2
	Other *	4		Other *	5		In-house	8
CaO	AS 1038.14.3	5	TiO2	AS 1038.14.3	5	SO3	AS 1038.14.3	5
	ASTM D3682	9		ASTM D3682	7		ASTM D5016	10
	ASTM D4326	15		ASTM D4326	15		ASTM D4326	12
	ASTM D6349	16		ASTM D6349	16		ASTM D6349	6
	Other *	4		Other *	4		Other *	7
MgO	AS 1038.14.3	5						
	ASTM D3682	7						
	ASTM D4326	16						
	ASTM D6349	16						
	Other *	3						
Ash Fusibility Parameters								
Reducing	ASTM D1857	23-24	Oxidising	ASTM D1857	19-20			
	AS1038.15	3		AS1038.15	3			
	ISO 540	10		ISO 540	10			
	Other stds**	1		Other stds**	2			
Trace Elements								
Co	ASTM D 6357	14	Ni	ASTM D 6357	15	Zn	ASTM D 6357	18
	In-house	5		In-house	10		In-house	6
	Other std methods**	2		Other std methods**	2		Other stds**	2
Cr	ASTM D 6357	18	Pb	ASTM D 6357	12			
	Inhouse	9		In-house	8			
	Other stds**	1		Other stds**	2			
Cu	ASTM D 6357	16	V	ASTM D 6357	16			
	In-house	5		In-house	6			
	Other stds**	2		Other stds**	2			

Other stds** = National and international standard test methods
 Other* =Other stds** & in-house methods

Disclaimer

To the extent permitted by law, ACIRS disclaims all warranties whether expressed or implied with regard to merchantability, non-infringement, or fitness for a particular purpose. In no event will ACIRS be liable for incidental damage or consequential loss arising from the use of this product.

Where the product does not conform to assigned property values, giving due consideration to the stated uncertainties and accepted tolerances, the total liability of ACIRS shall be limited at ACIRS' absolute discretion to either replacement of the product or refund of the purchase price.

Approval

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Table 4 Revision History

Document Name	Date	Comment
ACIRS-A1-TR-0 1	12/06/2016	Original
ACIRS-A1-TR-0 2	21/10/2021	Changes to uncertainties, definitions with inclusion of standard uncertainty