

## ADVANCES IN ASSESSMENT OF ODOURS FROM ALUMINA REFINING

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### Abstract

Odour emissions from alumina refineries can impact upon employees and neighbouring communities, with the significance of the impact dependent on the source of the odour, the point of discharge and the prevailing meteorological conditions. Of considerable importance to communities and employees that experience refinery odour emissions is an understanding of the substances that give rise to the characteristic refinery odour. However, measurement of chemical substances in ambient air often fails to detect substances that could be attributed to the prevailing odour.

A hybrid instrumental technique involving gas chromatography, mass spectrometry (GC/MS) coupled to an odour detection port has been used to study odours from alumina refineries. The volatile substances in the odours were separated by the GC and the effluent simultaneously directed to the MS analyser for identification and to the odour detection port for assessment by human nose. The intensity and character of the odours recorded by the assessor were correlated with the chemical speciation data to identify those substances that give rise to the majority of the odour. Odour thresholds have been determined for those substances to confirm the magnitude of their contribution to the total odour of the sample.

Results are presented that suggest a relatively small proportion of the volatile substances give rise to the odour from sources including digestion heater non-condensable emissions and calciner stack emissions.

### 1 Introduction

The effective management of odour emissions from alumina refineries requires a multi-faceted approach involving source measurements of odour emission rates, dispersion modelling to predict ambient odour impacts and field assessments to support the modelling predictions, as well as the installation of various emission control systems to reduce the emissions to acceptable levels. In addition to these technical measures, extensive employee and community consultation is necessary to ensure stakeholders have a realistic understanding of the issues. These efforts have produced significant improvements in odour emission performance at a number of Australian alumina refineries. However, refineries continue to emit low levels of the characteristic alumina refinery odour from the myriad of minor emission sources within the refinery as well as the large area sources such as residue disposal and cooling water lakes.

Some alumina producers have made extensive measurements of the composition of the emissions from the major emission sources. Complex mixtures of volatile organic compounds (VOCs) have been observed from digestion sources, with some VOCs also found in emissions from the calciners and coal-fired boilers.<sup>1</sup> Other emissions from vents and open process vessels also contain VOCs. Many of these VOCs are highly odorous, i.e. have low odour thresholds, and are considered to give rise to the characteristic odours from an alumina refinery. Inorganic gases such as SO<sub>2</sub> from combustion sources can also contribute to the refinery odour, typically when higher levels are emitted from combustion of high sulphur fuels.

A key component of the management of air emissions issues is the ability to identify the exact cause of the odour impacts that the employees and nearby communities experience. Field odour assessments and dispersion modelling of emissions from major sources can provide indications of likely sources and the magnitude of their impacts. However, they do not identify the chemicals that cause the

odour. Measurements of ambient air VOCs have been carried out, however, those measurements often fail to detect substances that could be attributed to the prevailing odour. As a consequence, the refineries can only infer the likely nature of the odour impacts based on the composition of the emissions sources. Unfortunately, this situation does not adequately address the workforce and community concerns, regardless of the fact that the measured ambient air concentrations are almost always well below occupational exposure and air quality standards.

To address this issue, the Alumina Industry Air Emissions Forum (AIAEF) has commissioned a project to investigate a new technology for direct measurement of odour character and intensity of individual VOCs from alumina refinery emissions. The AIAEF was established in 2003 to advance the industry capability in the management of air emissions issues common to all Australian refineries. The forum is comprised of the five Australian alumina producers<sup>2</sup> who provide funding for research programs, with administrative support from the Australian Aluminium Council. This paper describes the results from the initial work to evaluate this technology, including details of the optimised methodology and the findings from analysis of some alumina refinery odour samples.

### 2 Overview of the project

The technology evaluated in this project involves a hybrid gas chromatography mass spectrometry (GC/MS) system equipped with an odour detection port (ODP) to facilitate simultaneous instrumental analysis and odour assessment of individual VOCs in an emissions sample. In principal, this technique allows the identity and concentration of each substance to be measured and the relative odour intensity and odour character of that substance to be determined by human assessor without reference to published odour thresholds. This has the advantages that all substances in the emissions can be

<sup>1</sup>For this discussion, the term VOCs includes all organics with vapour pressures > 2 mm Hg at 20°C. This includes specific classes of volatile organics such as aldehydes, ketones, amines, alcohols, phenols, sulphides, thiols, carboxylic acids and hydrocarbons, which are generally reported separately from other VOCs. <sup>2</sup>Alcan Gove Pty Ltd, Alcoa World Alumina Australia, Comalco Alumina Refinery, Queensland Alumina Ltd and Worsley Alumina Pty Ltd.

assessed regardless of the availability of published odour thresholds or reference materials for determination of odour thresholds. Details of the instrumentation are provided below.

The primary objective of the project was to develop an appropriate method based on GC/MS/ODP instrumentation for the determination of odorous substances in refinery emissions. Key issues to address include the selection of appropriate odour sources (e.g. calcination, condensate, digestion emissions, residue disposal areas) for the development program, the selection of appropriate sampling techniques, the development of the analytical methodology for separation and identification of the odours. If feasible, odour thresholds would also be determined for substances identified as significant contributors to the odour of a particular source.

Samples of emissions from the digestion flash train (dump condensate flash pot stack), the digestion heater non-condensables vent and a (gas fired) calcination stack from the Worsley Alumina Refinery (Collie, WA) were used for this project, primarily due to the availability of resources to carry out the sampling and arrange transport to the laboratory. The development work was carried out by Leeder Consulting in their Melbourne laboratory, under the direction of the primary author. The Odour Unit (Sydney) provided specialist training for the assessment of odour intensity and odour character.

### 3 Methodology

#### 3.1 Odour sampling

Odour samples were collected in Nalophan odour sampling bags by either the bag in drum sampling technique (for neat samples) or using a syringe dilution technique developed by The Odour Unit (known as the SupaDiluta) for samples diluted with dry nitrogen. Samples were sent by overnight airfreight to the Leeder laboratories in Melbourne for testing. Although it is recognised that odour samples from some refinery sources can degrade and lose odour strength after sampling, it was not possible for this project to relocate the instrumentation and the operator to a location near to a refinery to facilitate immediate testing of samples. The exact chemistry of sample degradation is largely speculative, with the assumptions made that losses occur from chemical reactions including condensation, rearrangement, isomerisation and oxidation, as well as physical adsorption onto the walls of the bag. Highly volatile polar substances can also permeate through the Nalophan, with water readily lost from high moisture samples.

As a consequence, it is likely that the composition of the samples tested in this work will be slightly different to that in the emissions. However, those changes did not preclude the development of the techniques to identify the odorous substances, with the only limitation being the ability to accurately report the true concentrations of the substances in the samples.

#### 3.2 GC/MS/ODP instrument configuration

The measurements were carried out using an Agilent 6890 GC coupled to an Agilent 5973 MS with the column effluent split between a Gerstal ODP (2 mL/min) and the MS analyser (1 mL/min) for simultaneous detection and identification of the VOCs and assessment of the odours. Gerstal ODP software with voice recording capability was installed onto the Agilent Chemstation platform for processing of GC/MS and odour responses. The operator continually smells the effluent gases from the ODP during the chromatographic run and registers a positive response for odour detection via one of four buttons on a keypad. Selection of button 1 indicates a weak odour, buttons 2-4 indicate increasing intensity of odour response. The buttons are depressed for the duration of the odour peak and released when the odour is not detected. At the same time, the operator can describe the odour character and intensity in words that are recorded as an audio (.wav) file along with the ODP intensity plot. The timing of odour detection is recorded with the audio file for post-run reconstruction of the odour profile.

#### 3.3 Sample introduction

The odour samples are generally 15-25 L in volume, which is in excess of the capacity of a capillary GC instrument. Direct gas injection is limited to 10-100 mL of sample depending on the configuration of the

instrument and the particular analytes of interest. Also, preconcentration of the samples was likely to be required to achieve adequate sensitivity in the GC/MS and ODP analyses for low odour concentration samples. As a consequence, three techniques were evaluated for the transfer of the odour sample from the Nalophan bag to the GC/MS/ODP for analysis. These were:

*Direct injection* – samples injected using a gas tight syringe into a split/splitless inlet on the GC. Tested up to 100 mL injection volumes.

*Cryogenic preconcentration* – up to 5 L of the odour sample is passed through a U tube immersed in liquid nitrogen at 100 mL/min. The condensed material was warmed to room temperature and 100 mL of the concentrated headspace gases were injected into the split/splitless inlet on the GC. Highly volatile VOCs and some gases, in particular SO<sub>2</sub>, were expected to be captured by this technique.

*Adsorbent tube preconcentration* – up to 6 L of the odour sample was pumped through Tenax and Air Toxics adsorption tubes and thermally desorbed onto the GC column. Multiple tubes were prepared (each with 6 L of sample) and sequentially desorbed onto the column before analysis.

All of these techniques required cryocooling of the GC oven to trap the volatiles onto the head of the GC column to minimise band broadening during the separations.

#### 3.4 GC/MS/ODP conditions

A 30m x 0.25mm id x 1.0µm DB-624 capillary GC column (J&W) was used for the majority of the separations. This phase is optimised for separation of VOCs. A larger bore column (0.32mm id x 1.8µm DB-624) with was also tested to determine the benefits of increased capacity on the sensitivity of the analysis. The initial column temperature was maintained at -20°C for 3 minutes to trap the volatiles on the head of the column during the injection cycle (inlet at 150°C). A temperature program of -20-90°C at 20°C/min, then 90-200°C at 6°C/min and 200-250°C at 20°C/min was found to provide acceptable separations in a 30 min run time. Longer run times provide improved separations but the operator fatigue becomes a significant factor in the odour assessments. Column flow rate was 3 mL/min for the 0.25mm id column, with a 2:1 split between the ODP and the MS.

The ODP was configured with a humidified makeup gas flow (approx 20 mL/min) to the nose mask.

The identification of the VOCs was carried out by comparison of the mass spectra from the GC/MS chromatograms with spectra in the Wiley mass spectral database. As such, the assignments are tentative and will require confirmation by injection of authentic standards. The relative concentrations of the components were determined from peak areas, absolute concentrations were not determined in this work.

#### 3.5 Thermal desorption conditions

A Perkin Elmer ATD 400 thermal desorber was used for desorption of the adsorbent tubes. The Tenax tubes were desorbed at 200°C and the Air Toxics tubes at 280°C.

## 4 Results of method optimisation

#### 4.1 Direct injection

This was the most simple of the three techniques and was evaluated in the first experiments using condensate flash train and heater non-condensables samples. The odour concentrations in these samples were found to be very strong (101,000OU and 185,000OU, respectively) after dilution sampling. Injection volumes of up to 100mL were tested, however 25mL was found to be the practical limit that the instrumentation could handle.

The optimised conditions allowed the major components to be readily identified. However, the odour intensities from the ODP were only just perceptible, i.e. the concentrations were only just above threshold levels. As a consequence the assessment of the odours was difficult and a more concentrated sample was required to be presented to the instrument for odour detection. The technique was clearly unsuitable for the lower concentration calciner samples, which had odour concentrations around 2,000-4,000OU (neat samples).

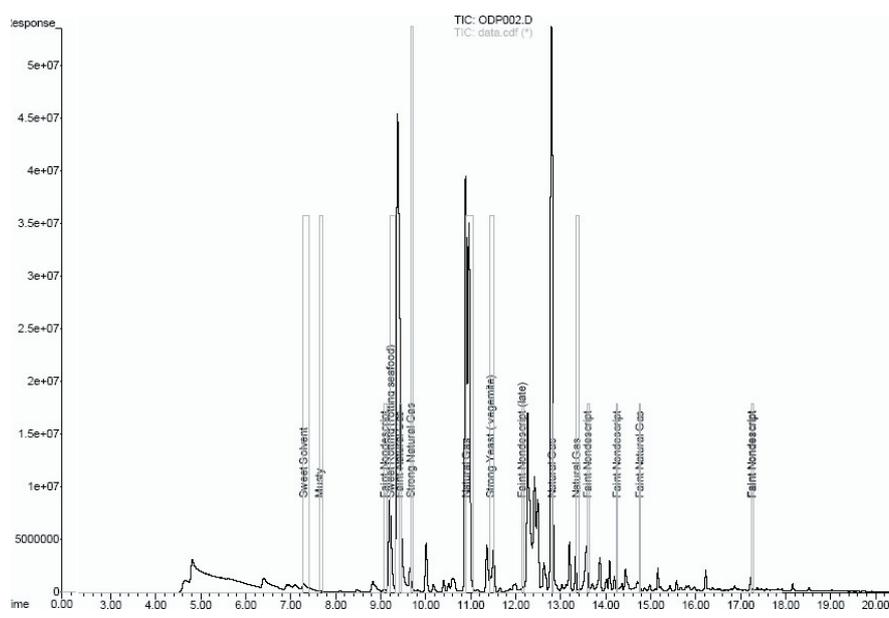


Figure 1. GC/MS/ODP chromatogram of digestion heater non-condensable emissions using cryotrap preconcentration

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#### 4.2 Cryogenic preconcentration

The initial tests of this method involved optimisation of the flow rate of the sample through the cryotrap (U-tube in liquid nitrogen). A flow rate of 100 mL/min was found to be optimal, with odours detected in the exhaust from the pump for higher flow rates after the sample was passed through the cryotrap. A 1.5 L subsample from a heater non-condensable odour sample was cryotrapped and 1 mL of the headspace from the cryotrap tube was injected into the GC/MS/ODP. This gave good separations for the majority of the components, with the exception of the early eluting substances. The odours for the peaks were more readily detected and the GC peak areas (relative concentrations) were increased compared with the direct injection technique, which reflected the increased amounts of the substances injected on the GC column. However, the intensities were still not as strong as required for reliable odour detection and additional preconcentration was indicated. As for the direct injection technique, the early eluting substances gave poor peak shapes, indicative of poor focussing of these substances on the head of the column. Figure 1 shows the GC/MS/ODP chromatogram for this sample. The squared top peaks represent the odour response and intensity. The poorly resolved peaks from 4.5-6.5 minutes are caused by instabilities in the MS analyser from residual permanent gases and water from the sample.

Cryotrapping preconcentration and GC/MS/ODP analysis of the low odour concentration calciner sample gave reasonable sensitivity for the later eluting substance but the peak shapes for the early eluting substances were much broader than before. Examination of the baseline spectra showed the presence of CO<sub>2</sub>, which was concentrated in the cryotrapping from the 5% CO<sub>2</sub> in the calciner gases. Normally, gases such as CO<sub>2</sub> are unretained on the GC column and do not interfere with the chromatography of later eluting compounds. However, the high levels in the headspace from the cryotrapped calciner sample were partially retained in the column at the initial oven temperature and resulted in an overloading of the stationary phase. As a consequence, cryotrapping is not a suitable technique for concentrating emission samples from combustion sources.

#### 4.3 Adsorbent tube preconcentration

The third technique evaluated in this study involved the adsorption of VOCs from the odour sample onto adsorbents (Tenax TA and Air Toxics tubes). This technique has the advantage that permanent gases

such as CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> as well as water vapour are essentially unretained which allows large preconcentration of the VOCs with negligible interferences in the GC/MS/ODP analysis. Up to 6 L of odour sample can be preconcentrated onto an adsorbent tube before breakthrough of the more volatile components becomes significant. The different adsorbents provide options for selectivity in adsorption of VOCs of different volatilities, with the Air Toxics tubes being more retentive than the Tenax tubes. The disadvantage of this technique is that the highly volatile VOCs are not quantitatively retained in the sampling or are incompletely recovered from the adsorbents during thermal desorption, which means the accuracy of the method for those substance can be reduced. However, these effects can be reduced by the use of adsorbents that are optimal for those substances.

Adsorbent tube preconcentration of heater non-condensables and calciner stack samples gave significant increases in MS response and odour intensities compared with the direct injection techniques and a moderate increase in responses compared with the cryotrapping technique. Figure 2 shows the chromatogram from desorption of a Tenax tube containing 1 L of heater non-condensables sample. There was a significant discrimination in responses for the two techniques, with later eluting VOCs enhanced for the adsorbent tube preconcentration (Figure 2) compared with the cryotrapping technique (Figure 1). Conversely, the cryotrapping showed higher odour intensities for early eluting peaks that were almost non-existent from the adsorption tube. These findings reflect the limitations in both techniques, where the adsorption efficiency is low for highly volatile substances on the adsorbent tubes and where the lower boiling (more volatile) substances are enhanced in the headspace from the cryotrapping.

#### 4.4 General comments on sample introduction

The results suggest a combination of cryotrapping and adsorbent tube techniques facilitates capture of the widest range of volatiles in odour samples to identify the odorous substances. However, it appears that the technique as currently developed is not optimal for the highly volatile (the lower boiling) substances, which are poorly focussed on the GC column from the cryotrapping technique. More work is required to resolve this issue, which might involve the use of a lower initial temperature coupled with a more retentive column phase to improve the chromatography of those substances.<sup>3</sup> The direct injection technique is only useful for very high odour concentration samples, and also requires improvements in the focussing of the lower boiling substances.

<sup>3</sup>The DB-624 column phase has a lower temperature limit of -20° C, so an alternative phase is required to facilitate lower initial temperatures.



Table 1: VOC and odour responses for a Worsley digestion heater non-condensables sample.

Substance (tentative identification)	Peak area	Odour Descriptor	Intensity
Acetaldehyde	Not integrated, very poor chromatography	Sweet solvent	1-2
Methane thiol	Not integrated, very poor chromatography	Faint non-descript	1
Trimethylamine	Not integrated, very poor chromatography	Sweet rotting fish smell	2
Furan	183148	Sulphur smell	1
Acetone	1264147	No odour detected	0
Dimethyl sulphide	774474	Sweet Rotting smell	2
1,3-Cyclopentadiene	37607100	Faint natural gas	1
Trimethylarsine	81239	Strong natural gas, garlic, metallic smell	3
Isobutanal	204395	No odour detected	0
2-Methylfuran	125893	No odour detected	0
2-Butanone	346062	No odour detected	0
Methyl-1,3-Cyclopentadiene	17031941	No odour detected	0
Cyclohexadiene isomer	12625341	Natural gas smell	2-3
Benzene	709814	No odour detected	0
2-Methyl-1,4-pentadiene	165919	Sharp, yeast , vegemite	2
Substance (tentative identification)	Peak area	Odour Descriptor	Intensity
4-methyl-2-pentene	150000	Faint natural gas smell	1
3-Pentanone	422479	No odour detected	0
Methylcyclohexane	157831	Strong natural gas smell	3
Methyl-1,4-cyclohexadiene	5852516	No odour detected	0
1,2-dimethyl-1,3-Cyclopentadiene	2033802	No odour detected	0
Methyl-cyclohexadiene isomer	3381321	Non descript	1
Methyl-cyclohexadiene isomer	2648996	Natural gas	2
Dimethyl disulphide	182909	No odour detected	0
2-Methyl-3-pentanone	100439	Non descript	1
Toluene	65283838	Metallic natural gas smell	1
2-Methylthiophene	137986	No odour detected	0
1,5-Dimethyl-1,4-cyclohexadiene	125463	No odour detected	0
2,4-Dimethyl-3-pentanone	585612	Strong natural gas smell	3
1,3,5-Cycloheptatriene	394125	Strong, sharp natural gas smell	3
Octatriene	439285	Sharp natural gas smell	2
1,2-Dimethyl-1,4-cyclohexadiene	1655285	No odour detected	0
1,2-Dimethyl-4-methylene-cyclopentene	1398645	No odour detected	0
Ethyl benzene	214377	Nondescript smell	1

m&p-xylene	1109244	Nondescript smell	1
trimethyl-1,3-cyclopentadiene	427290	No odour detected	0
1,2-Dimethylcyclohexadiene	214188	No odour detected	0
o-xylene	298550	No odour detected	0
C3 benzene	143832	No odour detected	0
Methylaurate	125436	No odour detected	0
C3 benzene	185549	Natural gas	1
Decane	321988	Medium natural gas	2
C3 benzene	145701	No odour detected	0
Trimethylbenzene	456637	No odour detected	0
Phenyl ethanol	231561	Savory	1
C4 benzene	144692	Yeast	1
C3 benzene	141290	natural gas	1
Undecane	267396	No odour detected	0
Methyl styrene	143398	No odour detected	0
C4 benzene	73052	Yeast	1
C4 benzene	94471	natural gas	1
Dimethylstyrene	55809	No odour detected	0
Dodecane	263115	Mowed Lawn	1
Dimethylstyrene	99637	Faint unpleasant odour	1
Methyl indene	123230	No odour detected	0
Methyl indene	131063	No odour detected	0
Tridecane	199150	No odour detected	0

The odorous components and more abundant non-odorous substances from the calciner sample are reported in Table 2. This shows only a small number of the substances contribute to the odour and the majority have odour thresholds above the concentrations presented from the ODP. The odorous substances appear to be mainly aldehydes and ketones (e.g. acetaldehyde, butenal, 3-buten-2-one, methylcyclopentenone), with some contributions from alkyl pyridines and tetrachloroethene. A number of odorous peaks were not identified due to their very low MS responses.

Table 2. VOC and odour responses for a Worsley calciner stack sample.

Substance (tentative identification)	Peak area	Odour Descriptor	Intensity
Acetaldehyde	~1000	Sweet solvent	1-2
Acetone	15987	No odour detected	0
Acetonitrile	8481	No odour detected	0
Butenal + 3-buten-2-one + 2,3-butanedione	6344	Faint non descript odour	1
2-butanone	11440	No odour detected	0
Ethyl acetate	12293	No odour detected	0
Tetrahydrofuran	6093	No odour detected	0
2-methylhexane	4762	No odour detected	0
2-methyl-1,3-dioxan	10061	No odour detected	0
Benzene	27287	No odour detected	0
3-methylhexane	11755	No odour detected	0
1-butanol	13978	No odour detected	0
Pyridine	10741	No odour detected	0
Toluene	70553	No odour detected	0
Tetrachloroethene	4330	Faint non descript odour	1
2-methylpyridine	~1800	Yeast	1
Xylenes	11494	No odour detected	0
2-Cyclopenten-1-one	10798	No odour detected	0
Not identified	~1000	Faint non descript odour	1
3-Heptanone	5368	No odour detected	0
1,3,5,7-Cyclooctatetraene	7004	No odour detected	0
2-ethylpyridine	~1000	Savory	1
2-methyl-2-cyclopentenone	6960	Savory	1
Decane	16400	No odour detected	0
Methyl styrene	9169	No odour detected	0
2-ethylhexanol	174986	No odour detected	0
Undecane	30021	No odour detected	0
Dodecane	70171	No odour detected	0
2,5-dimethylundecane	23844	No odour detected	0
2,6-dimethylundecane	52152	No odour detected	0
Tridecane	118633	No odour detected	0
Tetradecane	95387	No odour detected	0
Not identified	~2000	Faint non descript odour	1
Pentadecane	55608	No odour detected	0

## 6 Next steps

As indicated above, additional work is required to optimise the methodologies and unambiguously identify the odorous components using authentic reference standards. An improvement in the chromatographic conditions for the early eluting (low boiling) substances is required together with an evaluation of alternative adsorbents. Improvements in the sensitivity of both the cryotrapping and adsorbent tube preconcentration techniques are required for low odour concentration samples. The AIAEF have allocated funding in 2005 to investigate these issues and to further develop the technique.

## 7 Conclusions

A methodology has been developed to identify the odorous components of odour emissions from alumina refineries that involves chromatographic separation of the individual components on a gas chromatograph and simultaneous mass spectrometric analysis and human assessment of odour character and intensity. Two complementary sample introduction techniques that involve preconcentration of the volatile organic compounds from the odour samples provide reasonable sensitivity for odour detection of high odour concentration samples. The first technique involves cryotrapping and injection of headspace gases from the concentrate into the gas chromatograph, and the second involves trapping of the VOCs onto an adsorbent media and thermal desorption of the VOCs into the gas chromatograph.

Preliminary results from analysis of digestion heater non-condensable emissions have indicated that trimethyl amine, acetaldehyde, dimethyl sulphide, some of the cyclic unsaturated C5-C7 hydrocarbons, methylcyclohexane, and trimethylarsine are significant odour contributors with minor contributions from some aromatic and aliphatic hydrocarbons. The odorous substances from a gas fired calciner emissions appear to be mainly aldehydes and ketones (e.g. acetaldehyde, butanal, 3-butan-2-one, 2,3-butanedione, methylcyclopentenone) and some alkylated pyridines.

Further work is required to confirm these preliminary findings, in particular the identities and concentrations of the odorous substances. Improvements are required to increase the sensitivity of both the cryotrapping and adsorption procedures to increase the reliability of the assessment of low odour concentration emissions.

Note that none of the odours detected for individual substances were considered to have the characteristic wet cement odour that is typically used to describe the odour from an alumina refinery. This suggests that this odour is the result of the combination of the various odours from the substances in the emissions, and that no single substance is responsible for the characteristic alumina refinery odour.

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