

# LESSONS FROM 6 YEARS OF AUTOMATED WAD ANALYSIS

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## ABSTRACT

With growing adoption of the ICMI code, tightening discharge regulation, and heightened community awareness; measurement of WAD cyanide has become increasingly important to gold mine operation. The presence and demand for automated measurement of this parameter is steadily growing, as is the sophistication of the technology available to do so. This paper presents and discusses the lessons, developments and experiences in application of the OCM6000 WAD cyanide analyser over the 6 years since it was first introduced to the market. The initial configuration, its independent verification, and subsequently discovered limitations are used to open the paper, before a discussion of the factors that impact on measurement accuracy, reliability and how potential shortcomings are addressed both in the field and through design developments. The latest iteration of the analyser, with its increased accuracy, reliability and greatly reduced detection limit, is now suitable for applications that were previously reserved only for on-site laboratories. The paper concludes with predictions about future trends and applications for the technology, and some future configurations that are under development.

## INTRODUCTION

During the last decade, the International Cyanide Management Code (ICMC) has been adopted at an increasing pace (Breuer, Sutcliffe, & Meakin, 2010). Orica's Cyantific™ On-Line WAD Cyanide Analyser was developed in 2008 due to a need in the gold industry to measure and control Weak Acid Dissociable (WAD) cyanide in the mine effluents as required under the cyanide code. WAD cyanide includes cyanide species liberated at slightly acidic pH of 4.5 such as HCN(aq), CN<sup>-</sup>, the majority of Cu, Cd, Ni, Zn, Ag complexes and others that have a low dissociation constant ("Sample and Analysis, International Cyanide Management Code (ICMI) for the Manufacture, Transport and Use of Cyanide in Production of Gold (ICMI)," n.d.). WAD cyanide has been recognised as a very useful indicator of the toxicological impact of cyanide on the environment (Griffiths, Donato, Coulson, & Lumsden, 2014); hence ICMC compliance is based on minimising/eliminating impacts on animals (especially birds and marine animals) by measuring and controlling WAD cyanide (Donato et al., 2007) (Rumball, Munro, & Habner, 2007) (Hewitt, Breuer, & Jeffery, 2012).

This paper explores the discoveries and developments in the technology that have come from 6 years of field operation of the instruments by focussing on design considerations and how they have impacted on the operability and performance of the equipment.

## CYANIDE ANALYSIS METHODS

One important aspect of WAD cyanide analysis is the fact that reporting of WAD cyanide is method specific: it refers to cyanide species measured with specific analytical techniques, unlike free cyanide analytical methods, which identify the specific cyanide (CN<sup>-</sup>) species ("Sample and Analysis, International Cyanide Management Code (ICMI) for the Manufacture, Transport and Use of Cyanide in Production of Gold (ICMI)," n.d.). As such, analyses using differing techniques are not directly comparable.

ICMC accepts a number of methods to determine WAD cyanide in solution – below is a summary of the various methods available ("Sample and Analysis, International Cyanide Management Code (ICMI) for the Manufacture, Transport and Use of Cyanide in Production of Gold (ICMI)," n.d.):

Analyte	Method	Comments
Free Cyanide	AgNO <sub>3</sub> titration	Preferred method For process solutions primarily above 1 mg/l LQL: 1 mg/l HCN(aq), CN <sup>-</sup> , Zn(CN) <sub>x</sub> , parts of Cu(CN) <sub>4</sub>
	AgNO <sub>3</sub> titration with potentiometric endpoint determination	Alternate method Precise method of endpoint determination Measures same species as primary method
	Micro diffusion of HCN from static sample into NaOH [ASTM D4282]	Alternate Method Close to "free cyanide"
	Ion Selective Electrode	Alternate Method Close to "free cyanide"
	Direct colorimetry	Alternate Method HCN(aq), CN <sup>-</sup> , Zn(CN) <sub>x</sub> , parts of Cu(CN) <sub>4</sub> + ?
	Amperometric determination	Alternate Method Measures same species as primary method
WAD Cyanide	Manual distillation pH 4.5 + potentiometric or colorimetric finish [ISO/DIS 6703/2, DIN 38405 Part 13.2: 1981-02]	Preferred method LQL: 0.05 mg/l HCN(aq), CN <sup>-</sup> , Zn/Cd/Cu/Ni/Ag(CN) <sub>x</sub> Better results than ASTM method in presence of high copper concentration
	Amenable to chlorination (CN Total - non-chlorinatable part) [ASTM D2036-B, US-EPA 9010]	Alternate Method Measures same species as primary method
	SFIA in-line micro-distillation pH 4.5 + colorimetric finish [ASTM D4374]	Alternate Method Measures same species as primary method
	FIA In-line ligand exchange + amperometric finish [US-EPA OIA-1677]	Alternate Method Measures same species as primary method
	Picric Acid, Colorimetric determination	Alternate Method Measures same species as primary method
Total Cyanide	Manual batch distillation + titration/potentiometric or colorimetric finish [ISO/DIS 6703/1, DIN 38405 Part 13.1: 1981-02]	Preferred method LQL: 0.10 mg/l HCN(aq), CN <sup>-</sup> , Zn/Cd/Cu/Ni/Ag/Fe(CN) <sub>x</sub> , parts of Au/Co/Pt/Pd(CN) <sub>x</sub>
	SFIA, in-line UV irradiation, micro-distillation + colorimetric finish [ASTM D4374]	Alternate Method Measures same species as primary method

## FIRST ITERATION OF THE INSTRUMENT & ITS EARLY PERFORMANCE

### Measurement Method Selection & Evaluation

Due to its success in the existing OCM5000 Free cyanide analyser and status as the 'preferred' measurement for the ICMC, potentiometric titration was chosen as the final determination method for the WAD cyanide analyser. In order to convert the WAD CN into a form that is measurable by potentiometric titration, the laboratory technique described in ASTM 4500-CN I. *Weak Acid Dissociable Cyanide* (AphaAwwaWef, 1999) was adapted and automated.

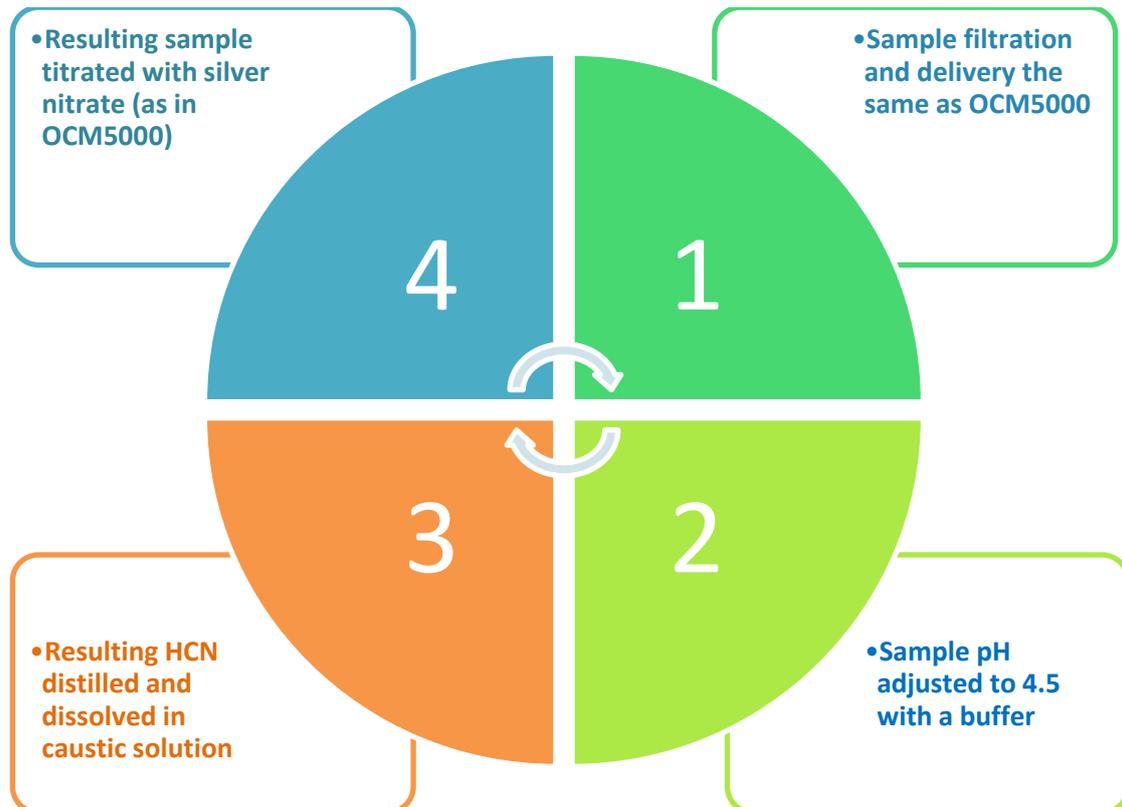
### ASTM 4500-CN I. Overview

The following key steps are performed in the laboratory method of ASTM 4500 I:

- The sample is modified (if necessary) to neutralise potential interferences
- A zinc acetate buffer is used to pH adjust the sample to between pH4.5-6 – converting WAD CN species to HCN and precipitating iron cyanide.
- The sample is distilled to volatilise the HCN(g), which is the adsorbed in a solution of caustic – generating a solution of NaCN
- The clean NaCN solution is then analysed using titration, with the measured CN being equivalent to the WAD CN in the original sample.

### Automated OCM6000 Measurement Overview

The standard configuration of the automated measurement contains four steps:



An additional step (1a) is available in the event of any interfering species that are not separated during the distillation stage.

This measurement method has since been successfully patented (US20110039347A1 ) and was chosen on the following basis:

- It is resistant to many interferences as the distillation step results in a 'clean' NaCN solution to analyse
- Reagents are cheap, readily available, and can be prepared by on-site laboratories
- It can be used in conjunction with silver nitrate titration finish as used in the Orica OCM5000 Free Cyanide Analyser
- The method allows a future development pathway to a total cyanide measurement while retaining the same platform
- Ability to reduce detection limit by increasing the ratio of sample size to receiver solution volume.

The first iteration of the Orica WAD Cyanide Analyser was evaluated by the Parker Centre in 2009. This study found that the instrument, in its configuration at the time, accurately measured WAD cyanide in the form of free cyanide, cyanide complexed to copper, nickel, and it successfully excluded the strong cyanide complex of iron. It was also found to be resistant to usual interferences from thiocyanate and sulphide due to the composition of the acetate buffer. It was concluded that the analyser had sufficient flexibility and adaptability to suit most mine sites' conditions.

## **What we found in the field / Operating Experiences & Improvements**

By the time the OCM6000 was released to the market, many sites were familiar with the operation and troubleshooting of the OCM5000 Free CN analyser. Positively, many sites understood the maintenance requirements associated with the unit and were able to successfully operate and maintain it for some time without issue. However, troubleshooting of the WAD analyser often focussed on knowledge of the free cyanide analyser and neglected the crucial differences between the analysers.

Although the architecture of the OCM6000 is based on the OCM5000, sharing many common parts, program sequencing, and the potentiometric finish; the OCM6000 is a much more complex instrument than OCM5000 hence troubleshooting the potentiometric titration section while ignoring pH adjustment and distillation was only dealing with one third of the process.

This was further compounded by the continual churn of metallurgists within the industry over the period since the analyser was released. Whilst the OCM5000 was installed on enough sites to have a reasonable amount of 'retained knowledge' within the industry, knowledge development surrounding the OCM6000 was hampered by constantly changing personnel on site. This has formed a crucial design consideration underpinning more recent developments in the technology.

A summary of the areas for improvement is contained below:

### **Equipment Layout & Troubleshooting**

The first iteration of the analyser focussed on function over form – the design aimed to get the process and measurement right over all else. With experience servicing and troubleshooting the instruments we identified the following concerns:

- Less-than-ergonomic access to manual controls: in the original design, water valves which control cooling water for the column and rinse water for the titration and mixing vessels, were placed behind the distillation column. That meant that they could only be accessed when the unit was powered off. The more we optimised the distillation, the more frustrating this was.
- Longer than necessary tube runs meant that the space on the unit wasn't optimised and the filtration system was placed under unnecessary stress in low p80/fine grind and/or high pulp viscosity applications

In isolation, these were minor issues; but in concert they impacted on the customer experience of the analyser.

Additionally, the first version of the instrument relied too heavily on retained knowledge for troubleshooting. It was reliable, but not bulletproof. So, in the event of a fault, more error messages were required to aid the troubleshooting. We approached the problem by analysing critical parameters that needed to be controlled for a trouble-free operation and reliable and accurate results. We then proceeded to introduce fail-safe mechanisms for the most common errors and where it was beneficial to the operation and ease of troubleshooting. Examples of additional checks, controls and interlocks that were identified over time and systematically patched are:

- Sample availability – A final check before commencing titration that helps to pinpoint errors in the event of troubleshooting
- Cooling water temperature and flow variability – Enhancing the control of the distillation stage
- Electrode (especially reference electrode) performance in regards to half-potential measurement – Early identification of the need to change or re-plate the electrode.

Rectification of these seemingly minor inconveniences has made the instrument significantly easier to troubleshoot and control. Future developments in these areas will be highlighted in the section "future developments"

## DETECTION LIMIT

### Early Experiences

The original OCM6000 was designed specifically for the 50ppm WAD cyanide discharge limit to tails dams, heap leach ponds and other open process ponds specified in the ICMC (Hewitt et al., 2012). Testing at the Parker Centre identified a practical lower detection limit of 3-4mg/l, but this was not deemed a critical parameter as many early installations were solely concerned with measuring to 50ppm.

It soon became apparent that the myriad of local environmental regulations experienced by our customers meant that some clients required WAD cyanide detection at much lower levels than ICMC's 50 mg/l (particularly Europe and parts of Asia), and a small number required the ability to measure and control total cyanide and not just WAD cyanide.

### Developments

Lowering the detection limit of the analyser required finding the boundaries and capabilities of the software, hardware and chemistry behind the analyser. As titration requires adding titrant in a series of defined 'steps' in order to determine the concentration of a species in solution, our focus was to look at ways of reducing the 'step' size, in order to accurately identify lower concentrations of CN. The first step was to sharpen the resolution by lowering the concentration of Silver Nitrate solution used within the analyser, meaning that every standard addition reacted with a smaller amount of cyanide. By making this simple change we were able to accurately measure a 1ppm standard solution of cyanide.

The second step was to alter the hardware associated with the analyser – the components that handled the process samples and the absorption after distillation. Making these changes allowed us to alter the ratio of sample size to caustic adsorption volume and further sharpened the resolution achievable. Fortuitously, the analyser control platform was designed with this flexibility built-in and hence software/sequencing adjustments could be made from the engineering menu.

At sub-1ppm levels, control of the distillation unit becomes even more critical than with regular WAD measurement, as even a small amount of CN that is not absorbed in the caustic solution can create a relatively large variation in results – significantly impacting on the accuracy of the instrument. Improvements to the distillation process are covered in the subsequent section 'distillation'.

A recent run of experiments has been conducted at a client's site as part of the commissioning to test the performance of the analyser at 0.5ppm CN, yielding the following results:

Settings:

Standard [CN<sup>-</sup>] = 0.5 mg/L

Results of 10 consecutive runs:

Run No.	V of AgNO <sub>3</sub> (mL)	[CN <sup>-</sup> ] (mg/L)	Peak size (mV)
1	1.00	0.52	64
2	1.09	0.57	61
3	1.00	0.52	66
4	0.98	0.51	64
5	0.98	0.51	66
6	1.01	0.53	63
7	0.92	0.48	65
8	0.91	0.47	64
9	1.00	0.52	68
10	0.98	0.51	67

Average = 0.51 ppm

Standard Deviation = 0.026

Relative standard deviation = 5.0%

A blank was also tested at the same settings reporting 0.16 ppm.

The 'peak size' represents both the size and consistency of the titration endpoint – in this case showing a clearly defined and repeatable endpoint. These results show that the instrument is very consistent at analysing WAD cyanide concentrations around 0.5 ppm, while the minimum detectable concentration at these settings is about 0.2 ppm.

## **DISTILLATION & COOLING**

### **Early Experiences**

Over the life of the analyser, the distillation has proved to be the most important stage of the measurement process, and the most susceptible to variations in site process conditions that are not captured on specification sheets.

The distillation of the pH adjusted sample requires all the HCN in the sample to reach the titration cell as vapour, while retaining all the water (and other interfering species) in the boiling pot. The original design was robust for a range of different process chemistries, but it didn't address variability in site services; something which turned out to have a much greater impact on the analyser's performance.

Whilst the analyser specification sheet specifies 1 – 5 bar water pressure as an essential service for operation of the unit, potable water on mine sites is usually used by many systems that can alter its availability. For example, Potable water is periodically used by the gold room or cyanide dissolution systems, which drops its pressure in some locations around the process plant and in some cases severely limits its availability. Its temperature can also vary significantly with ambient temperature between day and night time and between summer and winter (potable water is sometimes pumped around the plant in black poly pipe in direct sunlight). This variability was outside the original design scope and has been a key area to address in our development of the technology

The variability creates 2 potential problems:

1. If cooling is not sufficient (due to low water flow or high temperature), then water vapour (from the sample) can get through the column and settle in the tube between column and the titration vessel, or even condense in the titration vessel. This can transfer various species into the titration vessel, which can then interfere during silver nitrate titration (double-peak distributions), while moisture on the walls of tubes can also affect the results by absorbing cyanide gas.
2. If cooling is too efficient, cyanide gas will condense before the titration vessel (either in the column or in the tubing), which lowers results significantly.

### **Developments**

Once the potable water consistency was identified as an issue, these problems were successfully solved by inclusion of a recirculated and heated water system, which provided cooling water for the analyser at constant temperature and flow. It draws water from the mains, when needed, to maintain constant level, and its volume provides a necessary buffer for periods when potable water is not available at normal pressure. It also successfully smooths out temperature fluctuations by providing water above the HCN boiling point, allowing all the HCN vapour to make it into the caustic solution for

adsorption and analysis. This system is still an add-on to the existing unit, but it will be fully integrated into future versions of the instrument (see: Future Developments). Additionally, the heating (and control) hardware associated with the distillation circuit has been upgraded to provide faster and more reliable distillation.

Once this change occurred, it became apparent that the two issues outlined above accounted for the vast majority of reported analyser performance problems. The platform has since shown itself to be significantly more reliable and accurate in the field.

The improved performance of the distillation unit also helped drop the detection limit below 1 ppm with a few additional modifications, mainly an increase in sample size, which required an increase in volume of the heater section of the distillation column, and a decrease in receiver caustic volume. It also became apparent from a number of experiments that the cyanide peak size during the potentiometric titration is dependent on the concentration of the receiving caustic solution. Its concentration was optimised to give the highest peak, while still providing excellent performance in absorbing HCN.

### **Interferences & Other Unexpected Events**

No discussion of cyanide measurement is complete without analysis of potential interferences. This is especially important for WAD cyanide measurement as the reported result depends on the method applied. On release, we were mindful of the fact that although the instrument was deemed resistant to common interferences, it couldn't have possibly encountered the full range of complex solutions generated in CN detox systems like peroxide, INCO and Caro's Acid.

The distillation system has proved very robust at avoiding interferences – with a couple of suspected interferences subsequently shown to be issues related to sub-optimal cooling in the distillation circuit. Although the instrument platform has the ability to add measurement step '1a' to remove interferences, we have not yet had a confirmed instance where additional reagents or program steps were necessary.

However, two situations have been encountered that bear discussion in this paper:

- On one operation that uses both Caro's acid and an INCO (SO<sub>2</sub>/Air) detox system, a precipitate was present in the filter and sample tubing, which interfered with analysis and in severe circumstances, could even prevent sample flow into the unit. We suspected that the problem was caused by 1) a very small size of the precipitate formed during cyanide detox reaction, 2) an incomplete reaction between the SMBS, oxygen and cyanide due to insufficient availability of oxygen, which was then provided by our instrument when back flushing the filter with compressed air and causing precipitate formation in the filter, and 3) both mechanisms happening simultaneously. The solution was a smaller aperture filter coupled with an air-less backflush system, which used solution to backflush the filter by pumping it back and not using compressed air. Other measures, like placing the sample point slightly later in the process after the INCO tank where the reaction is more likely to be complete, are being investigated. Our findings as to the cause of the precipitation prompted the site to increase capacity of their oxygen system, so they can improve efficiency of the INCO system by providing it with more oxygen.
- We had one instance of a report of intermittent lower-than-laboratory (Picric acid method) results in Caro's Acid samples from one of the Australian sites. Investigation in collaboration with CSIRO was inconclusive, but it was speculated that excess peroxide from the Caro's acid reaction consuming cyanide during the distillation phase. Whilst the interference appeared to disappear with an upgrade to the distillation column (indicating a heating/cooling

problem), further R&D is required to investigate the relationships between these processes and automated WAD cyanide measurement.

Over the years of analyser servicing, we have also come across some 'unexpected' incidents that have kept the service team on their toes. Such as:

- A site reporting inconsistent analysis results was found to have a distillation column full of precipitate, probably formed due to insufficient cooling water. A separate cooling water system was installed to counteract potable water flow and temperature variations.
- After much frustrating troubleshooting, the cause for a consistent variance between lab results and analyser results was found to be an error in preparing the silver nitrate solution.

## FUTURE DEVELOPMENTS

From current trends, the environmental constraints put on gold mining with cyanide will likely continue to strengthen with time. Already some jurisdictions consider ICMC limits as not sufficient, for example the 50 ppm WAD cyanide limit on discharges to tails dams has been reduced to 10 ppm WAD cyanide in Europe (Laitos, 2012). Some clients consider total cyanide as a better predictor of environmental impact, as in Thailand, where total cyanide is used in discharge limits ("Kingsgate Consolidated Limited - Sustainability," n.d.). To be able to adapt to the strengthening constraints, miners will need to, among other measures, be able to control cyanide effluents to a much lower concentration than currently. This means two things:

- ICMC will be adopted in more mining operations than currently – either directly or via the requests of regulators
- Cyanide effluent limits will gradually become more strict

Both measures will increase the cost of gold production, so mining companies will respond by continuing to introduce practices that will minimise the costs such as installing lower cost cyanide detox processes and improving control of cyanide addition and detox reagents. In terms of cyanide analysis all these changes will mean increasing use of and reliance on cyanide measuring equipment, lower detection limits and in addition to analysis of free and WAD cyanide, total cyanide.

We are planning on addressing these issues via our technology by:

- Installing an upgraded analyser control platform (expected release mid 2014) to improve performance in the following areas:
  - Quicker (and remote) customisation of analyser sequencing to deal with process changes
  - Improved visible information / error display and data access for site troubleshooting
  - Easier output of historical data for analysis and/or remote troubleshooting
  - Control and monitoring of more functions, allowing for finer control and measurement
- Further lowering the detection limit of the analyser to 0.1ppm WAD CN and below, then validating with operating experience; encroaching further and further on territories previously reserved for analytical laboratories with all the benefits that automated analysis at real-time brings
- Adapting the platform to provide total cyanide measurement – a relatively simple modification from the existing process.
- Inclusion of more controls to clearly identify errors when they occur and allow for immediate corrective action with minimal troubleshooting

A collaborative research and development project is currently underway to further investigate potential interferences and practical limits to the detection limit, readying the analyser to measure even lower concentrations of cyanide in solution.

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