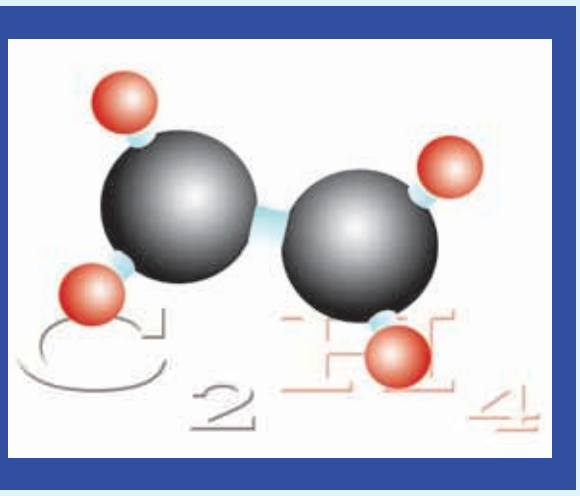
Analysis of Impurities in Polymer-grade Ethylene, Propylene and 1,3-Butadiene

by Surinder (Sandy) Thind



Abstract:

Producers of high purity monomers need to measure, not only, more and more impurities in their high purity product, but also, they need to measure these impurities at lower and lower detection limits. This paper describes the latest technique available to perform these analyses at low ppb levels with high levels of accuracy and speed. Both laboratory and on-line detection is possible.

The Critical Nature of Impurity Analysis:

The production of poly-ethylene and poly-propylene has become a very competitive business. Producers utilize more selective and more sensitive polymerization catalysts all the time. These catalysts are very expensive, and frequent replacements may lead to a loss. During catalyst replacement, the plant is shut down, which further adds to losses. In order to avoid frequent shutdowns due to catalyst poisoning, these companies insist that monomer producers meet tight specifications regarding such poisonous impurities. Failure to comply can result in lawsuits and loss of business. For this reason, impurity analysis has achieved critical importance.

Non-Hydrocarbon Impurities That Require Monitoring:

Just one of the impurities listed in Table 1 has the power to adversely affect many polymerization catalysts, yet more than one of these may be present during the process. For this reason, monomer producers must be able to accurately detect and measure one or more of the specified impurities at very low levels.

Impurity	Typical Specification
Arsine	Less than 20 ppb
Phosphine	Less than 20 ppb
Ammonia	Less than 100 ppb
Hydrogen Sulfide	Less than 20 ppb
Carbonyl Sulfide	Less than 20 ppb
Nitrogen Dioxide	Less than 50 ppb
HCN	Less than 100 ppb
HCL, HF	Less than 200 ppb
Phosgene	Less than 50 ppb
Sulfur Dioxide	Less than 50 ppb
Chlorine	Less than 30 ppb

Table 1: Typical Impurities That Require Monitoring in Monomer Production

Current Detection Techniques – A Case Study with Arsine:

Take as a case study the detection of one impurity: arsine in olefins. Even at low ppb levels, arsine can adversely affect certain polymerization catalyst properties and also lead to polymer contamination.

Detection of arsine in ethylene, propylene, or 1,3-butadiene is very difficult at the desired 5 ppb level. Normally, a complicated GC column system is used to separate arsine from propylene. After this separation of low ppb levels of the impurity from almost 99.9% propylene, expensive systems such as GC-AED, are used to these ppb levels of arsine. Since GC-AED will also respond to ppb or ppm levels of other impurities, such as hydrogen cyanide, nitric oxide, ammonia, or hydrogen chloride. This being the case, with many other impurities present at low ppb levels, it is easy to misidentify the arsine peak. Thus, the individual working with GC-AED must be highly skilled. Even the most experienced chemists experience difficulty in positively identifying and accurately quantifying low (1-10 ppb) levels of this impurity. As a result, most companies have stopped using this technique for arsine detection and have gone back to the 'old' wet technique method, which requires hours of bubbling followed by detection via atomic absorption.

The manual laboratory technique and the GC-AED technique for ppb-level arsine detection are only available for laboratory testing applications to date. Further, both of these techniques are not only impractical for on-line applications, but they are also very expensive to install and maintain. It is clear that, in today's monomer-production facilities, non-specialist technicians must be able to quickly, efficiently, and accurately perform arsine analysis without GC separations both either in the lab or on-line.

It is at this point that the time-proven analytical technique of Dry Colorimetry draws new attention. The application of the dry colorimetric technique to the measurement of trace arsine in the hydrocarbon streams has been independently demonstrated by several petroleum/petrochemical companies. Figure 1 indicates potential monitoring points in an olefin/polyolefin plant for trace arsine measurements. With prompt, reliable on-line results, the process control engineer has the opportunity to develop strategies to minimize the effect of a periodic excursion in arsine levels.

In one field test, the concentration of arsine was monitored before and after an arsine scrubber. Wet chemical analysis was used to obtain the concentration of arsine, 25 ppb and 0 ppb, respectively. The results obtained using Dry Colorimetry technology corresponded to the wet chemical results within experimental error.

A New Look at Dry Colorimetry: INTRODUCTION

Classical colorimetry utilizes an impinger to collect gas in a liquid medium. Chemical reagents are then added to the medium to cause it to change color in proportion to the concentration of gas present. The resulting color change is measured by a laboratory spectrophometer and compared to known standards.

Ultra-sensitive "tape" detectors, are also colorimetric based, but these are dry reaction substrates that serve as gas collecting and analyzing media. Individually formulated for a specific gas or family of gases, each detection tape is a non-toxic, proprietary chemical reagent system. When exposed to a target gas, the tape will change color in proportion to the amount of gas: the higher the target gas concentration, the darker the stain that will appear.

The change in color, or stain, on the tape is read by a photo-optical system in the analysis instrument, and the intensity of this stain is then compared to a standard response curve preprogrammed into the instrument's data system.

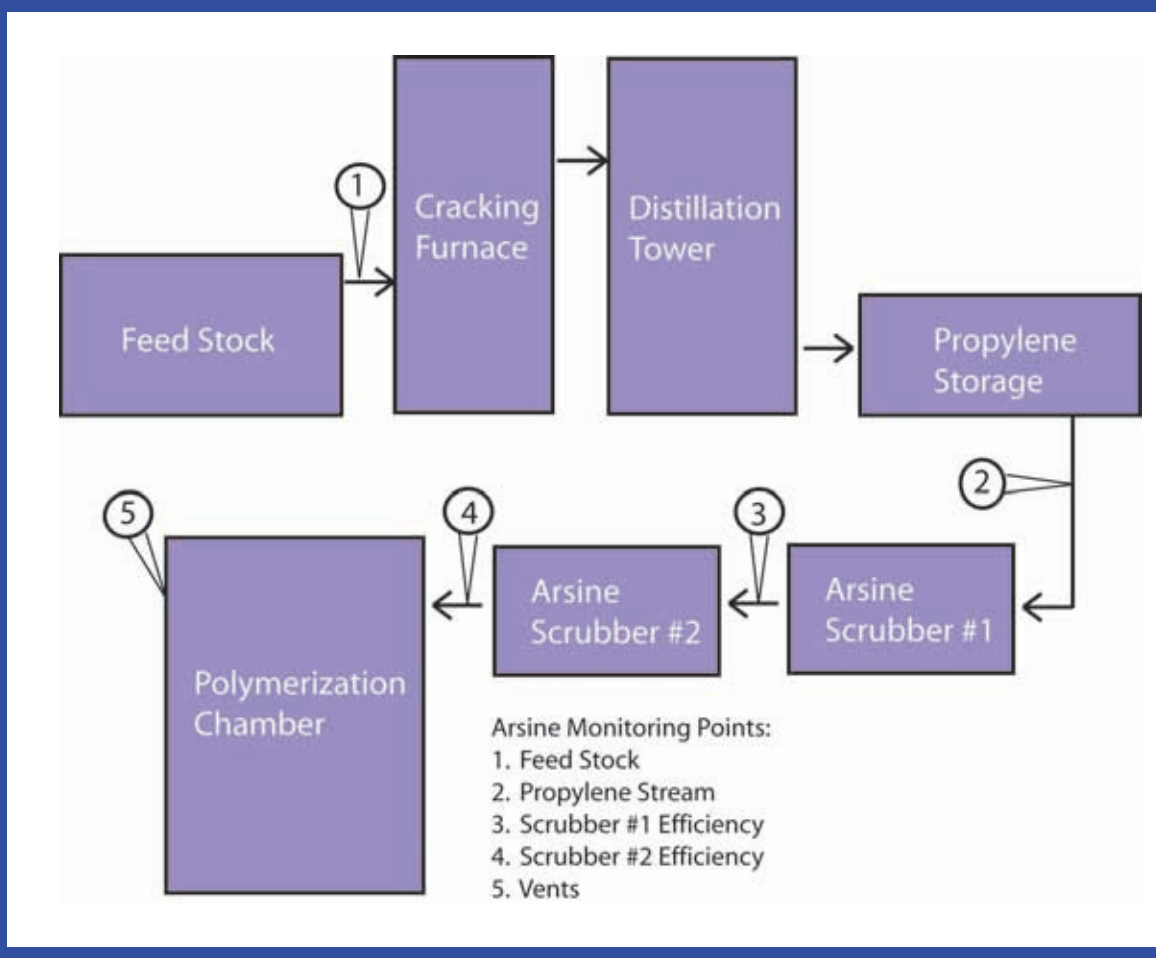


Figure 1: Some Potential Monitoring Points for Arsine in an Olefin /Polyolefin Plant

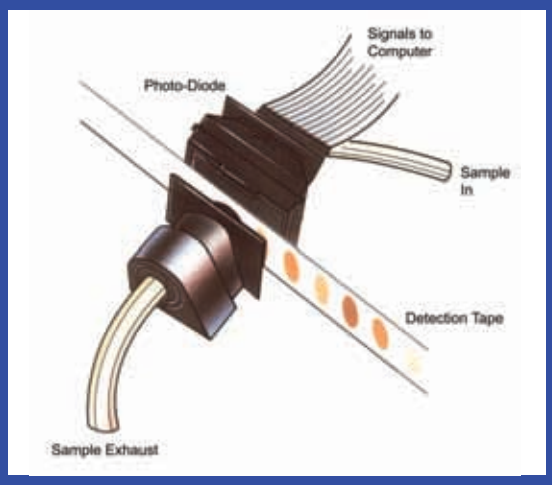


Figure 2: Modern Dry Colorimetric Detection: The C.I. Analytics System

Analytical Technique

During operation, the detection tape is incremented through a sampling "window" where it is exposed to a metered sample stream. If the target gas is present, a stain proportional to the concentration develops. Simultaneously, a beam of light is reflected off the exposed portion of the tape and the intensity of this light is measured continually. As the amount of reflected light decreases due to stain development, the reduction is sensed by a photocell detector as an analog signal. This signal is converted to a digital format, matched to the gas response curve stored in the analyzer's permanent memory, and displayed/ documented as the actual concentration value. All of these functions are microprocessor controlled and, in the best cases, carried out by a complete computer.

The use of this spectrophotometric technique, in combination with microprocessor/complete computer control, provides excellent accuracy, repeatability, and detectability of low ppb (parts-per-billion) concentrations.

Gas	Concentration as Determined by Standard NIOSH Methods	Analyzer Reading (ppb)
AsH3	23	22
	49	47
	99	100
HF	5.0	4.0
	10.1	9.7
	19.5	19.7
	24.5	26

Table 2: Dry Colorimetric Results as Compared to Those of NIOSH Standard Methods

Accuracy of Dry Colorimetry

The dry colorimetric detection technique, as outlined above, gives accurate and extremely precise results. Factory calibration of instruments and the detection tape is referenced against NIOSH approved and analytical methods. Both laboratory and field tests have verified that analyzers using Dry Colorimetry give data in agreement with standard reference methods, as typified by the examples in Table 2.

Key Benefits of Dry Colorimetry for Impurity Analysis in Monomer Production:

It has been demonstrated that low-level impurity analysis is of crucial importance for those involved in high-purity monomer production. Instruments operating on Dry Colorimetry that are designed for low-level impurity analysis, such as those pictured in Figures 3 and 4, offer producers the following key benefits:

- Each of the proprietary detection tapes reacts instantly to the target gas for fast results that are visible due to the color reaction. For example, it takes less than 90 seconds to detect and measure ppb levels of ammonia without use of any GC columns.

- Dry colorimetric detection is very sensitive, allowing for low-level analysis of different toxic gases that must be identified in process streams at ppb levels for subsequent removal.

- Dry Colorimetry is also very specific to the gas that the detection tape is designed to measure. It will not react to other substances (solvents, hydrocarbons, etc.) often found in process streams or other samples. As a result, expensive downtime due to false alarms is virtually eliminated.

When configured accordingly, an impurity analysis instrument operating on Dry Colorimetry also offers the following:

- detection and quantification, with a single analyzer, nearly every non-hydrocarbon impurity on the product specifications sheet for monomers, including:
  - o difficult to analyze arsine at 1 ppb level
  - o HCN and ammonia at low ppb levels

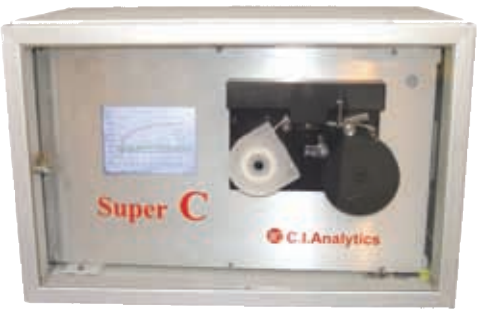


Figure 3: C.I. Analytics superC Multi-Element Analyzer Detects up to 8 Impurities in up to 6 Streams

Figure 4: C.I. Analytics Model 8510 Process Gas Analyzer for Monitoring One Specific Impurity in On-Line Applications

- reliability
- unmatched accuracy at ppb levels
- simple to use by non-technical staff:
  - o no GC separations and no complicated set ups
  - o clear, unambiguous results that require little interpretation: if the instrument operates with a complete computer and proprietary software, the "Peak", as it elutes, can be displayed on the screen, and a numerical concentration value can be viewed
- laboratory or on-line use, depending upon instrument area classification

Conclusion

Low level impurity analysis, even to low ppb levels, is increasingly crucial to ensure high-quality product and minimization of catalyst poisoning during the monomer-production process. Current techniques utilized for such detection are expensive, require a high-level of technical expertise, and are generally highly maintenance intensive.

Taking another look at Dry Colorimetry, it becomes clear that this is the ideal technology for carrying out required low level impurity analysis in the monomer production industry. Producers should look for a high-quality, dry colorimetric, impurity analysis instrument, such as those in Figures 4 and 5, to ensure that their end product is of high quality and that expensive catalysts are protected during the process, both of which subsequently ensure the integrity of a company's bottom line.

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