The formation of the phosphorus trichloride from phosphorus and chlorine

Key Issues

- Highly corrosive, reactive and toxic reaction mixture
- Detection limits for reactants and products better than 1%
- Composition required every 5 minutes

Introduction

Phosphorus trichloride (PCl_3) is an important raw material used in the production of commercial oxy-phosphorus compounds. Examples include phosphate esters, oil and polymer additives, special lubricants, pest control compounds, fire resistant materials, etc. The trichloride is produced by the direct chlorination of elemental white phosphorus (P_4). The process, which is exothermic, proceeds as a continuous reaction. Phosphorus is added to a boiling mixture of the trichloride and phosphorus, while a continuous stream of chlorine is added to the reactor. Control of the phosphorus-to-chlorine ratio is important to maximize the yield of the product, to ensure that the correct amount of heat is generated, and to maintain the stoichiometry for the production of the trichloride. Sufficient heat is generated by the reaction to distill the product as it is formed. Heating and feed rates are also important to minimize the formation of an undesirable byproduct - phosphorous pentachloride (PCl_5). A typical reactor configuration for PCl_3 production is shown in Figure 1.

Reaction summary

$P_4 + 6Cl_2 \rightarrow 4PCl_3 + \text{Heat}$	Product
$PCl_3 + Cl_2 \rightarrow PCl_5 + \text{Heat}$	Byproduct
$P_4 + 6PCl_5 \rightarrow 10PCl_3 + \text{Heat}$	Uncontrolled heating

Over time, there is a buildup of contaminants, mainly introduced via the phosphorus feed. This requires that the reactor be shut down periodically for cleaning. Prior to this, it is necessary to purge the system of the pyrophoric phosphorus. This is accomplished by adding just sufficient chlorine to react with the phosphorus, while ensuring that not too much is added, thereby reducing the formation of the byproduct. The chlorine flow must be terminated at the point where all the phosphorus is consumed. In order to maintain the critical balance in the reaction, both during production, and during the shutdown process, it is necessary to monitor the reaction with a tool that is both sensitive to changes in composition, and is capable of relatively fast feedback.

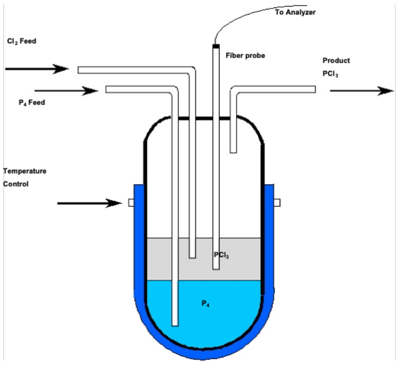

Figure 1: Reactor for PCl_3 production

ⓘ All Raman analyzers and probes referenced in this application note are Endress+Hauser products powered by Kaiser Raman technology.

Experimental

The basic ingredients of the reaction are chemically reactive, highly corrosive, and are difficult to analyze, even under normal conditions. The standard laboratory methods of analysis are based on chromatography or wet chemistry; a titration with elemental bromine in a halogenated solvent. These methods give a partial picture relative to the condition of the reaction, by providing information on only the free phosphorus (pyrophoric, P_4) content. They are also labor intensive and time consuming, and neither method provides measurement for the phosphorus chlorides, PCl_3 and PCl_5.

The elemental chlorine, reaction intermediates, and the reaction products are corrosive, reactive, and toxic materials. Many of these materials react readily with moisture to form hydrochloric acid. This places special demands on the nature of materials that come into contact with the reaction mixture. Ideally, the measurement should be made within the reactor, without the need to transfer the material. Also, because of the issue of chemical reactivity, material selection for any optical probes is particularly difficult. Demands are placed here on the materials used for fabrication of the probe, including the window materials.

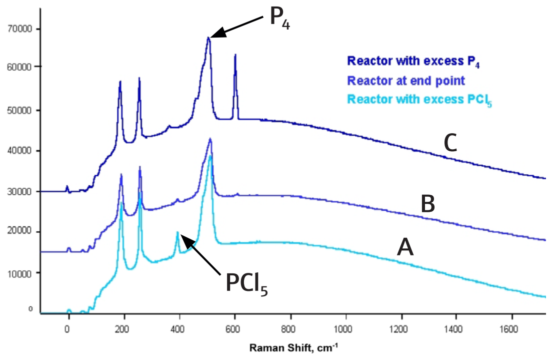

Figure 2: Raman spectra of PCl_3 reaction mixture (B) and PCl_3 spiked with P_4 (C) and PCl_5 (A)

All of the materials, including the phosphorus, have characteristic Raman signatures with unique bands that may be used to monitor each of the components. Infrared methods are unsuitable because of the inability to measure elemental phosphorus, and because of the difficulties associated with sampling, which includes the lack of a remote fiber optic interface.

Results and discussion

The example presented here features data was obtained from a Raman analyzer system equipped with a 785 nm diode laser. Spectra from reactor-grade (“black”) phosphorus trichloride, spiked with PCl_5 (A) and phosphorus (C), are shown in Figure 2. The 606 cm^{-1} band is used for monitoring the presence of free phosphorus, and a band at 393 cm^{-1} is used for the PCl_5. A fiber optic insertion probe, featuring a 9-around-1 bundle was used; 400µm inner fiber for excitation and 200µm outer fibers for collection. Some interference from the Raman silica background from the fibers is experienced but this does not constitute a problem for the measurement of phosphorus or the phosphorus chlorides. Furthermore, the silica Raman signature is sufficiently reproducible to permit its subtraction from the measured spectra of the reaction mixture. Good quality, measurable spectra, with adequate sensitivity, are obtainable within a 0.5 minute timeframe.

Conclusions

Raman spectroscopy is the only practical instrumental method for the on-line monitoring of the continuous reaction between phosphorus and chlorine in the formation of phosphorus trichloride. No other optical spectroscopy technique can provide either the information on the components of interest – P_4, PCl_3 and PCl_5 – and/or can provide the ease of sampling in this non-ideal, hazardous and corrosive environment. The technique responds in a sufficiently short timeframe to provide feedback for the control of the process. It is used to indicate the progress of the reaction, and it reports the concentration of each of the components, with a sensitivity of <1% by weight.[1]

References

1. Gervasio, G.J. and Pelletier, M.J., “On-line Raman Analysis of PCl_3 Reactor Material,” *Journal of Process Analytical Chemistry*, Vol. III, No. 1&2, **Fall 1997**.