

# Safety Improvement of Chemical Processes Involving Azides by Online Monitoring of the Hydrazoic Acid Concentration

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## Abstract:

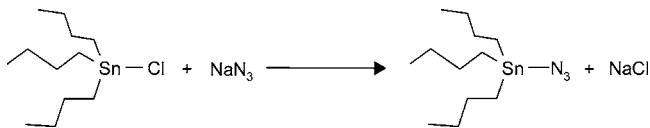
Hydrazoic acid (HN<sub>3</sub>) is formed during the synthesis of tributyltin azide and in the following cycloaddition to prepare a tetrazole ring compound. The formation of this substance is inherent to many azide processes because small amounts of protic components cannot be avoided. Hydrazoic acid is a very toxic volatile compound, which has highly explosive properties. Under certain conditions (presence of impurities in the reaction mixture), the gas concentration can come close to the decomposition limit. Therefore, online monitoring of this gas concentration is essential to ensure the process safety. FT-IR and FT-NIR experiments were performed in the laboratory scale to calibrate the spectrometers. Due to the possibility of using quartz light fiber cables, a FT-NIR spectrometer was installed to monitor the hydrazoic acid concentration in the industrial scale.

## Introduction

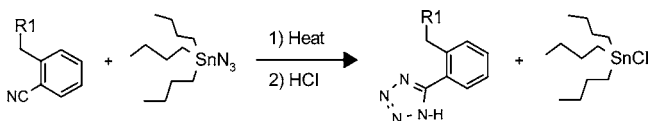
The synthesis of tri-*n*-butyltin azide from tri-*n*-butyltin chloride and sodium azide (Scheme 1) is a well-known reaction in the chemical industry.<sup>1</sup> The principal industrial applications of trialkyltin compounds include biocides in marine antifouling paints, fungicides, herbicides, insecticides, miticides, and antifeedants in agriculture. Tri-*n*-butyltin azide is also of some importance as a reagent for the preparation of pharmaceutical tetrazole compounds<sup>2–4</sup> (Scheme 2). In recent times, many new syntheses and applications of organic azides has been published.<sup>5</sup>

The formation of hydrazoic acid is inherent to many azide processes because small amounts of protic components cannot be avoided (impurities in tri-*n*-butyltin chloride and presence of some water or strong mineral acid such as hydrochloric acid). This compound was first reported by Curtius in 1890.<sup>6</sup> The protic compound will react with tri-*n*-butyltin chloride to form hydrochloric acid (Scheme 3).

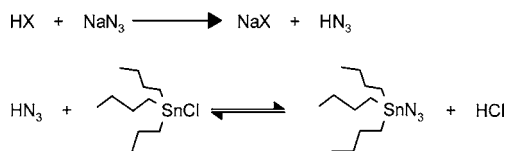
## Scheme 1. Synthesis of tri-*n*-butyltin azide



## Scheme 2. Cycloaddition of tri-*n*-butyltin azide to a nitrile to form a tetrazole ring compound



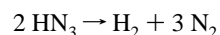
## Scheme 3. Postulated mechanism of the formation of hydrazoic acid in presence of protic components



Hydrazoic acid, as well as sodium azide and tri-*n*-butyltin compounds, is highly toxic.<sup>7</sup> These substances are known to produce hypotension in laboratory animals and humans, and to form strong complexes with hemoglobin and consequently block oxygen transport in the blood.

Acute inhalation of HN<sub>3</sub> vapor by humans results in lowered blood pressure, bronchitis, eye, nose, throat, and lung irritation, headache, weakness, and collapse.<sup>8</sup> The recommended airborne exposure limit is 0.11 ppm as hydrazoic acid or 0.3 mg/m<sup>3</sup> as sodium azide, which should not be exceeded at any time.<sup>9</sup>

Hydrazoic acid has a boiling point of 36 °C and is therefore considered as highly volatile under process conditions. It is an unstable component which may decompose violently, forming nitrogen and hydrogen according to:



Depending on the literature source, an explosive gas mixture can be formed with air or nitrogen above a concentration of more than 8–15%.<sup>10–12</sup> In the presence of some impurities

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which are sometimes present in the raw materials,  $\text{HN}_3$  concentrations up to 6% were measured during the development of the process. To ensure the process safety, concentrations of gaseous hydrazoic acid that are too high must be avoided, and the concentration level must be continuously known during the reaction. The maximum allowable concentration determined during the process risk analysis corresponds to one-fourth of the lower explosion limit, i.e., 2% (assuming a limit of decomposition of 8%). Recently, a series of tests were performed to determine the lower explosion limit more accurately, and the results of this work will be published in a separate paper. The explosion and decomposition behavior of hydrazoic acid in the gas phase has been investigated in a 5-L explosion sphere equipped with a continuous spark with an energy of approximately 10 J (ignition source). The temperature was varied between 50 and 150 °C, the partial  $\text{HN}_3$  pressure between 40 and 200 mbar, and the absolute initial pressure of the gas mixture between 57 and 1000 mbar. Within the temperature and pressure range investigated, the lower decomposition limit of  $\text{HN}_3$  in nitrogen lies between 10 and 16 vol %.

The concentration determination in the gaseous phase was done in the past by using UV spectrometry after reaction of a sample with sodium hydroxide (sample handling and preparation).

Due to the dangerous properties of hydrazoic acid, any sampling and contact with this substance should be avoided for the analytics. Therefore, an online determination of the  $\text{HN}_3$  concentration must be developed to avoid any hazardous excessive concentration. The results of an online monitoring system may be used to take steps against a further unwanted release of  $\text{HN}_3$ , such as cooling of the reaction mixture or flushing the reactor headspace with nitrogen.

The aim of this paper is to describe the possibilities of online monitoring of the concentration of the very toxic and explosive hydrazoic acid in the gas phase to improve the safety and the hygiene for the operators during chemical processes. The method developed at the laboratory scale should be robust, accurate, and useable on an industrial scale. Moreover, a productivity increase can be expected due to the elimination of the waiting time for the results of the classical UV analysis in a laboratory. An important benefit of online monitoring of  $\text{HN}_3$  gas is the fast alarm in case of unexpected gas release.

**Synthesis Procedure.** Laboratory experiments with hydrazoic acid should be performed under closed conditions to avoid any contact with this substance. Moreover, it is recommended to wear personal protective equipment such as a gas mask and hearing protectors during the handling of hydrazoic acid (e.g. during cleaning operations).

*Synthesis of Tri-*n*-butyltin Azide.* Tri-*n*-butyltin chloride was charged in a stirred reactor, and the reaction system was inerted with nitrogen. Sodium azide was added, and the contents of the reactor were heated to the process temperature. The reaction mixture was stirred at the same temper-

ature until the reaction was completed. Then, the reaction mass was cooled to 25 °C.

*Cycloaddition To Form the Tetrazole Ring Compound.* A nitrile compound was added to the tri-*n*-butyltin azide reaction mixture at 25 °C. Then, the reaction mixture was heated up to the process temperature and stirred until the reaction was completed.

**Technical Solutions.** The potential of  $\text{HN}_3$  online monitoring was evaluated in the laboratory scale. Mid-IR and NIR spectroscopy were tested to determine the most adequate solution for an industrial application.

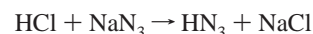
**Instruments.** The FT-IR (Mid-IR) spectroscopic online measurements were carried out with a ReactIR 1000 instrument (Applied Systems) equipped with a gas cell with a 10-cm path length. The lens of this cell is made of zinc selenide ( $\text{ZnSe}$ ) and its body of Hastelloy C276. This spectrometer operates according to the Fourier transformation method, and its spectral region is between 650 and 4000  $\text{cm}^{-1}$ . The experimental conditions consisted of resolution, 8  $\text{cm}^{-1}$ , and number of scans, 64.

The FT-NIR online measurements were performed with a Matrix F spectrometer (Bruker) equipped with a 10-cm path length transmission gas cell for the laboratory feasibility study and a 30-cm path length cell for the industrial scale. The lens of the cell is made of sapphire and its body of titanium. The experimental conditions consisted of resolution, 8  $\text{cm}^{-1}$ , and number of scans, 20. The spectral region investigated with this method is between 4000 and 12000  $\text{cm}^{-1}$ .

The gas cells of both spectrometers were heated with an electrical device for the laboratory experiments; the one for the production plant was equipped with a thermostated double jacket. This heating is required to guarantee isothermal measurement conditions and to avoid the condensation of hydrazoic acid (pure hydrazoic acid in liquid form is also highly explosive; faint vibrations are enough to initiate detonation) or of a solvent in the cell during the completion of the synthesis reactions.

These gas cells were installed in a loop where the gas phase was circulating using a pump. Preliminary tests have shown that the concentrations in this loop and in the reactor headspace are identical.

**Calibration in the Laboratory.** Hydrazoic acid gas that was needed to calibrate the spectrometers was prepared in laboratory scale by the addition of sodium azide to a hydrochloric acid solution:



Gas samples were taken in the reactor headspace using a syringe through a septum and, after absorption in a 1 N sodium hydroxide solution, were analyzed using UV spectrometry (wavelength 250 nm) and ionic chromatography to determine the sodium azide concentration (and therefore deduce the hydrazoic acid concentration). A calibration model was developed using the partial least-squares<sup>13</sup> (PLS) multivariate analysis method (chemometrics). This model is

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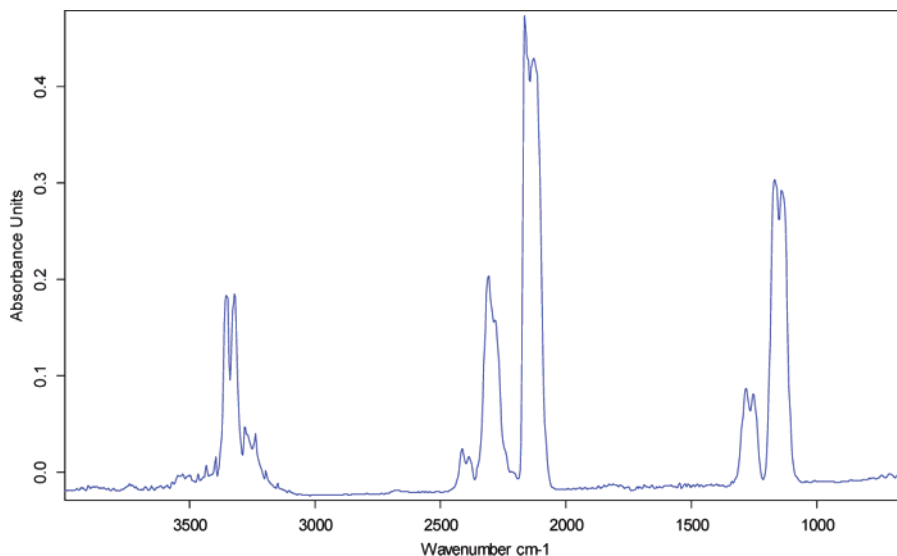


Figure 1. FTIR spectrum of hydrazoic acid vapor at 85 °C.

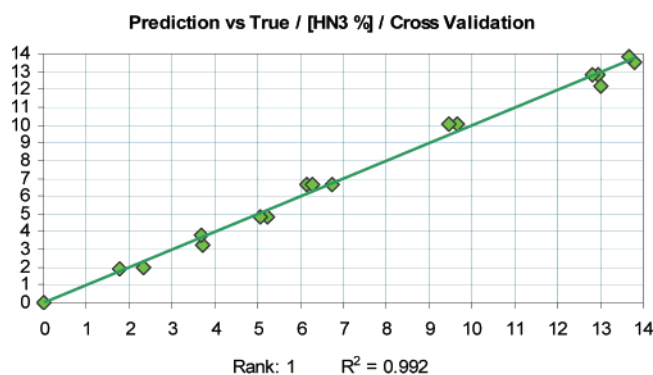


Figure 2. Cross validation for the determination of the concentration of hydrazoic acid (FTIR).

the calibration function used for the analysis of unknown samples. Before using the model for routine application, its prediction capability was tested (validation).

**Results for FTIR.** The measured spectra show the typical bands corresponding to the fundamental vibrations of the molecular bonds<sup>14,15</sup> (see Figure 1, spectrum measured at 85 °C). The frequencies of the main peaks are summarized hereafter:

NH stretch, $\nu(\text{NH})$	3323 and 3354 $\text{cm}^{-1}$
NNN asym. stretch, $\nu_{\text{as}}(\text{N}_3)$	2131 and 2165 $\text{cm}^{-1}$
NH bend, $\delta(\text{HNN})$	1255 and 1285 $\text{cm}^{-1}$
NNN sym. stretch, $\nu_{\text{s}}(\text{N}_3)$	1143 and 1170 $\text{cm}^{-1}$

The results of the cross validation are shown in Figure 2.

Figure 3 shows the FTIR spectra of the gaseous phase during the whole synthesis of tri-*n*-butyltin azide. Mid-IR is an adequate method for online monitoring the hydrazoic acid concentration during the chemical process.

**Results for NIR.** The measured NIR spectra show bands corresponding to the overtones of the molecular vibrations (see Figure 4, spectra at different concentrations varying between 1.5 and 6 vol %).

The results of the cross validation are shown in Figure 5 (RMSECV is the root-mean-square error of cross validation, and  $R^2$  the determination coefficient).

These results show that NIR is also an adequate method to online monitor the hydrazoic acid concentration during the investigated chemical reactions.

**Transfer of the Method to the Industrial Scale.** Both spectroscopic methods (Mid-IR and NIR) could be used to monitor online the concentration of hydrazoic acid in the gaseous phase during the synthesis of tri-*n*-butyltin azide and the subsequent cycloaddition to form a tetrazole ring compound. Due to the following advantages of the NIR spectrometer, it was decided to implement this method in the industrial plant:

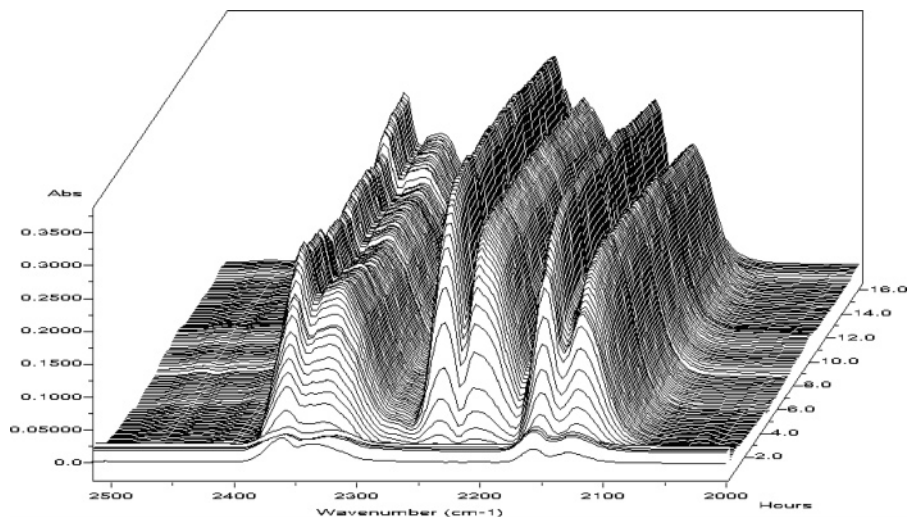
(1) remote measurements over long distances using light fibers (the spectrometer can be installed in an explosion safe room). The installation of the spectrometer in a control room is easier than in the production hall. Only very short light fibers are actually available for Mid-IR; contrariwise, standard quartz cables can be used over several hundred meters with NIR.

(2) NIR spectrometers are often equipped with a multiplexer which allows to use a device with several probes. The chosen spectrometer can simultaneously measure concentrations at six different points, some of them can be from a different process. Some Mid-IR spectrometers can be equipped with a multiplexer, but the final price of the equipment is not comparable with that of a NIR device.

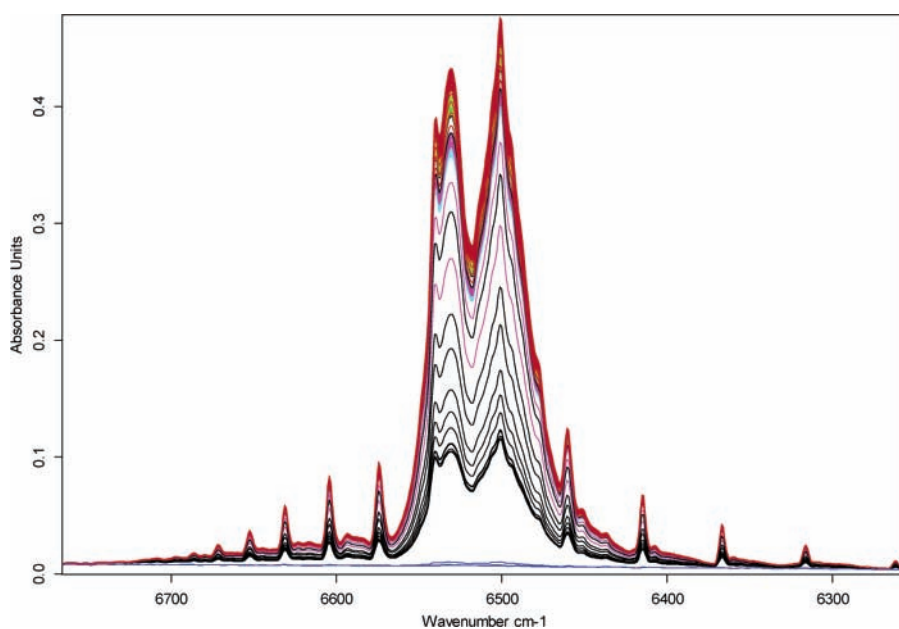
Corrosion tests were performed with titanium; they show that this metal is compatible with  $\text{HN}_3$ . Hastelloy C276 was only used during the feasibility study with FTIR in the laboratory scale: no visible corrosion was observed during these tests. Nevertheless, no real corrosion tests were performed with this metal; therefore, Hastelloy C276 cannot be considered as adequate for long exposure times. The only metal present in the actual plant installation is titanium (the reaction is performed in a glass-lined steel reactor).

The hydrazoic acid concentration was first monitored online in a 630-L reactor in a pilot plant during the

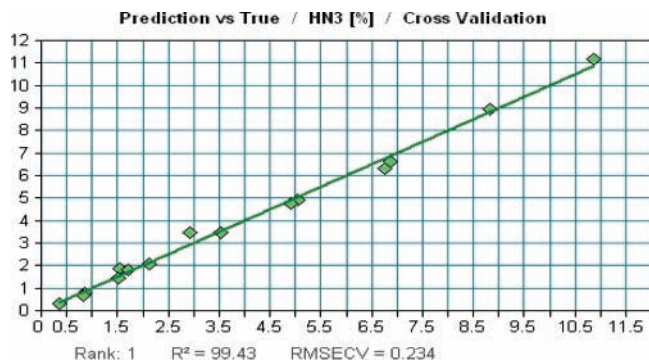
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**Figure 3.** FTIR spectra of the gaseous phase during the whole synthesis of tri-*n*-butyltin azide.



**Figure 4.** NIR spectra of hydrazoic acid (concentrations range 1.5–6 vol %).



**Figure 5.** Cross validation for the determination of the concentration of hydrazoic acid (NIR).

completion of both reactions. The measured concentrations were below the maximum admissible concentration of 2% which was defined during the process risk analysis (see Figure 6). Different process steps can be distinguished in this graph:

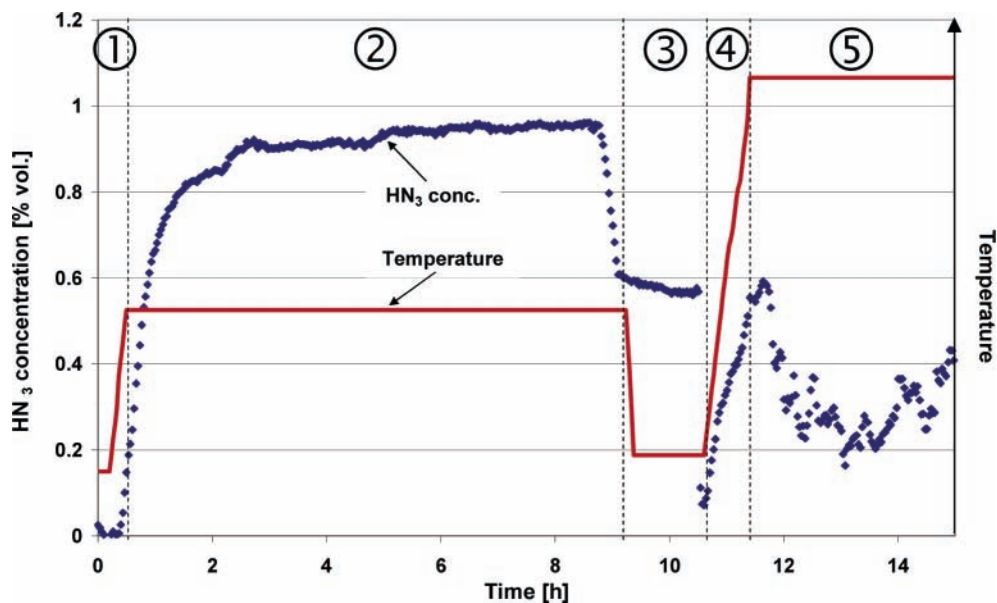
(i) Synthesis of tri-*n*-butyltin azide: heating of the reaction mixture up to the process temperature. The generation of hydrazoic acid starts slowly during this temperature ramp.

(ii) Stirring period at the same temperature: during the completion of the reaction, the hydrazoic acid concentration increases progressively and reaches a maximum value of about 0.95% (vol).

(iii) After the cooling of the reaction mixture to 25 °C, the nitrile compound is added to the reaction mixture. Lower hydrazoic acid concentrations are measured during this addition (0.55–0.60%).

(iv, v) Temperature ramp up to the process temperature and stirring period at this temperature: lower concentrations are registered during these process steps (between 0.20 and 0.60%).

All of these results are in good accordance with the results of the traditional analytics which were performed simultaneously to verify the accuracy of the model.



**Figure 6.** Concentration of hydrazoic acid during the completion of the syntheses in the pilot plant.

In case of an unexpected increase of the  $\text{HN}_3$  concentration (e.g. due to the presence of traces of acidic impurities) measures were defined during a detailed risk analysis to ensure the process safety. The main recommendations are the following:

(1) If a  $\text{HN}_3$  concentration increase is observed, heating should be interrupted. Excessive  $\text{HN}_3$  gas-phase levels may be reduced by flushing the headspace with a gas that is inert to the caustic scrubbers.

(2) The condenser system should be turned off during the reaction phase. This measure avoids formation of highly explosive liquid  $\text{HN}_3$  condensates if there are excessive  $\text{HN}_3$  levels in the gas phase.

(3) The presence of any heavy metal must absolutely be avoided.

(4) It has to be physically impossible to charge strong acids (e.g., hydrochloric acid) to the reactor through existing lines.

Hydrazoic acid is quite safe in dilute solution<sup>16</sup> (<17%). The concentration in the reaction mass is below this value. Concentrated or pure hydrazoic acid is violently explosive. Therefore, the reactor headspace, the loop with the gas cell, and the condenser are heated above 40 °C to avoid any condensation of  $\text{HN}_3$ .

After the successful demonstration of this technique in the pilot plant, the method was transferred to larger production plants (4000 L reactor) to ensure an optimum process

safety. Similar results were registered on this industrial scale.

### Conclusions

This work shows that the concentration of the very explosive hydrazoic acid gas can be monitored using online NIR with a good accuracy. The results as well as the equipment for the different development phases (from the laboratory to the production plant) are presented. Using this technique, sampling of the very toxic gas phase can be avoided. Moreover, monitoring the  $\text{HN}_3$  concentration in the reactor headspace is an additional measure to minimize the probability for an explosion of  $\text{HN}_3$  vapors in the large-volume production plant. This real-time concentration monitoring leads to a significant improvement of the process safety and of the hygiene conditions for the operators. Moreover, the spectrometer can be simultaneously used for monitoring the concentration in several reactors due to the utilization of light fibers (different processes can be run in these reactors).

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