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INVESTIGATING AN ACCIDENT USING REACTION CALORIMETRY

On the early 2007 a fine chemicals' company near Barcelona had an accident involving the generation of toxic gases. Eight people suffered different degrees of intoxication, showing evident cyanosis. The synthesis reaction was reproduced using the Mettler-Toledo RC1 showing important thermal effects, and the generation of important amounts of gas at the last steps of the process. The gas was finally identified by GC-MS as methyl nitrite.

It is well known that lack of knowledge is the main cause of accidents in the chemical industry [1]. However, many small chemical industries continue working with a very limited knowledge about the processes they are carrying out. Investigation of accidents is a key tool to avoid their reiteration in an industry. Dissemination of the results is a contribution to avoid the occurrence of accident similar to those investigated. On the early 2007 a fine chemicals' company near Barcelona had an accident involving the generation of toxic gases. Eight people suffered different degrees of intoxication, showing evident cyanosis. Two of them were found laying on the floor at a filtration area separated by a door from the reaction area. Other six of them were affected when they tried to help the first two victims or at the exterior of the facilities. Our group at the IQS-URL was commissioned by the Catalan Government to investigate the causes of the accident. After considering different hypothesis, only one of the processes carried out in the facilities could generate toxic gases capable to produce the observed symptoms. Such a process was the preparation of an inorganic salt using both methanol and nitric acid. As a consequence, nitrogen oxides (NOx) were pointed as the most probable responsible agents of the intoxication. The initial communications from the personnel of the company to media indicated nitrogen oxides as the responsible substances with no doubt. The objectives of this paper are describing both the investigation procedure of the accident, and the lessons learned from it.

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Tab. 1 - Measured heats of reaction

Step	kJ/kg
Metal oxide solution	20
Methanol dosing	203
Maturation	73
Nitric dosing	186

Results and discussion

The synthetic process considered consisted in fourth steps:
1) preparation of an aqueous solution of a metal oxide
2) reduction of the metal using an excess of methanol
3) formation of the nitrate salt by addition of concentrated nitric acid
4) evaporation of water to allow crystallisation.

Such process had been performed approximately once a year along the last years, but in a different plant to which had the accident. None at laboratory or industrial scale significant generation of gases had been noticed. Only some important heat generation both during methanol and nitric dosing had been reported. However, the sentence "it never happened nothing" is the most dangerous symptom that a real risk exists, and that an accident could be ready to happen.

The inspection of the industrial facilities demonstrated that certain amounts of reddish-brown nitrogen oxides were retained in different vessels attached to the reactor in which the reaction was carried out. However, and despite this fact and the initial suspicions concerning nitrogen oxides, when our team started the investigation some weaknesses of such a hypothesis were disclosed:

- nobody noticed estrange odours in the production area during the period of the accident;
- no red-brownish colour was observed in the air during the accident period;
- some persons were affected out of the production area without noticing any odour.

Nitrogen oxides appear to be innocent.

Carbon monoxide could be another candidate. However, it has a molecular weight lower than air, so it was highly improbable to cause the observed effects taking into account the geometry of the production plant.

An important point to be considered is the air flow in the facilities. The reaction area had no forced ventilation. Air flow to avoid accumulation of dangerous vapours and gases was established opening a big gate, which communicated the reaction area with the exterior of the building. At the opposite wall of that gate, there was a door communicating to the filtration area. Such door should be shut during operation, but it was usually open. Other holes in the wall communicated both areas.

The filtration area communicated to a workshop through a door usually closed, but let open during the accident time. The workshop communicated to the exterior of the building.

Witnesses indicated that the air flow the day of the accident was from exterior to reaction area, from it to the filtration area, and finally to the exterior through the workshop. This fact explains the location of the affected persons: two in the filtration area, and six at the exterior, just at the opened external door of the workshop.

Moreover, a question remained open: what was the generated toxic chemical, and why?

The synthesis reaction was reproduced using the Mettler-Toledo RC1® showing important thermal effects (Tab. 1). The methanol reaction (Step 2) showed the most important heat evolution, and a strong accumulation of unreacted materials [2, 3]. So, it should be performed with exquisite care. Dosing of nitric acid is also associated to a strong heat generation, but reaction appears to be instantaneous. As a consequence, heat generation is controlled by the dosing rate. No significant gas generation was noticed up to this point (Fig. 1).

However, generation of important amounts of gas was evident during the final concentration step. The gas had no reddish-brown colour, and it did not generate this colour in contact with air. So, nitrogen oxides could be discarded as responsible of the observed health effects.

The content of CO in the evolved gas was monitored using a Dräger-type system. Only very small concentrations were detected.

The gas was finally collected and analysed by gas chromatography and mass spectrometry (GC-MS) at the Analytical Chemistry Department of the IQS - Universitat Ramon Llull. One of the main components of the gas was methyl nitrite. The agent of the accident had been identified.

Formation of methyl nitrite is easily understood by reaction between the excess and methanol and nitric acid, possibly catalysed by other components of the reaction mass.

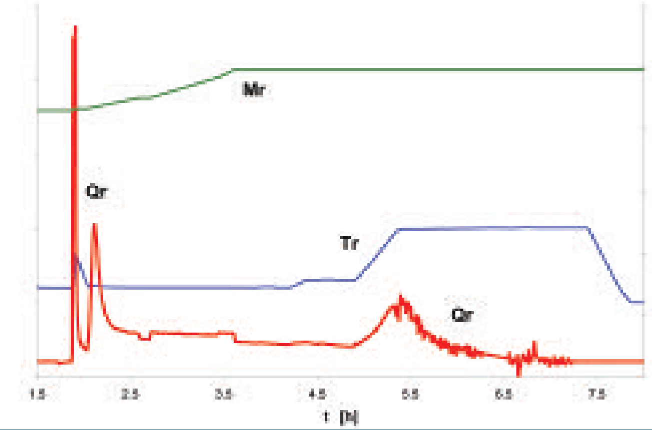

Fig. 1 - Heat evolution during the reaction with methanol. The ordinate values have been suppressed to preserve confidentiality

According to Bretherick's [4], many alkyl nitrites are thermally unstable and may readily decompose or explode on heating. Methyl nitrite explodes more violently than ethyl nitrite.

A new lesson is learned: mixing methanol and nitric acid is described by Bretherick's [4] as potentially explosive, but it is not indicated that new highly toxic and explosive substances are also generated.

Incidents involving alkyl nitrites and affecting health are not estrange. Just an example from TOXNET [5] describes as in 1994 two workers from the same factory presented to the same emergency department within six weeks of one another with moderate (Case 1) and severe (Case 2) methemoglobinemia.

It was, once again, a case of lack of knowledge. The use of simple methodologies such as *HarsMeth* [6-8] as proposed by the European network *HarsNet* [9] can help to detect dangers and to prevent risks in the chemical industry, especially in SME. Many of the accidents could be prevented just thinking a bit on what chemistry is involved in a process, and how this is performed.

Conclusions

The accident was caused by a lack of knowledge combined with poor environmental conditions, such as natural instead forced ventilation.

The investigation of the accident led to identify the toxic agent implied in the accident. Its formation was not expected, but it does not correspond to any estrange chemistry. Methyl nitrite had been produced probably all times the process was carried out, but it was not detected.

Reaction calorimetry is the most powerful technique to study chemical processes at bench scale. So its possibilities must be disseminated, and its use must be strongly recommended.

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ABSTRACT

Studio di un incidente mediante l'uso di un calorimetro di reazione

Agli inizi del 2007 è accaduto un incidente in un'azienda di chimica fine vicino a Barcellona, che ha generato gas tossici. Otto persone sono state colpite dalle esalazioni e hanno mostrato diversi livelli di intossicazione, fino alla cianosi. La reazione di sintesi è stata riprodotta usando un apparecchiatura Mettler-Toledo RC1, riscontrando rilevanti effetti termici e la formazione di elevate quantità di gas durante gli ultimi stadi del processo. Mediante GC-MS il gas è stato identificato come nitrito di metile.