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Determination of nitrate content in whey and milk powders at a dairy after an occupational accident with nitric acid

by Olle Nygren, BSc¹

NYGREN O. Determination of nitrate content in whey and milk powders at a dairy after an occupational accident with nitric acid. *Scand j work environ health* 8 (1982) 227-230. A case of accidental occupational intoxication by fumes of nitrogen oxides and the application of an indirect method for the analysis of nitrate, nitrite, and nitro groups to establish the origin of the intoxication are presented. The method is based on the formation of a copper neocuproine complex, and extraction of the complex with methyl isobutyl ketone. The amount of copper in the organic phase is directly proportional to the nitrate content. This copper complex is determined by atomic absorption spectrophotometry. The results, which showed that samples from the contaminated workroom contained 0.1-0.2 % nitrate, while blanks contained less than 0.02 %, strongly support the hypothesis proposed for the course of the accident.

Key terms: atomic absorption spectrophotometry, copper neocuproine nitrate complex, determination, nitrogen oxides.

Nitric acid reacts vigorously with organic materials, with the evolution of fumes containing mainly nitrogen oxides (3). The composition of these fumes depends on such factors as temperature, humidity, and the nature of the organic material. Nitrogen oxides primarily affect the alveolar system, forming nitric and nitrous acids in the presence of oxygen. The acids formed are irritants, causing congestion of the throat and bronchi and edema of the lungs. As the oxides are only slightly soluble in water, they act as minor irritants to the mucous membranes in the upper respiratory tract. It is therefore possible to inhale dangerous amounts of the oxides before any real discomfort is noticed. The inhalation of high concentrations causes irritation of the nose and throat, but these symptoms disappear when fresh air is breathed. However, some 6-24 h after exposure a sensation of tightness and burning in the chest develops. Dyspnea and shortness of breath may increase rapidly, followed by cyanosis, loss of consciousness, and in some cases

death. If recovery from the pulmonary edema occurs, there is usually no permanent disability.

In many cases it may be very difficult to ascertain whether an accidental evolution of nitrogen oxides has occurred once the reaction has ceased and the fumes have cleared away. Standard nitrate or nitro tests (2) often prove to be unsuitable because of the complexity of the sample matrix. Infrared spectroscopy usually proves to be inadequate as well, since the complex organic matrix often contains too much water to give a high enough resolution of the spectra, and thus interpretation is impossible. An indirect method for the determination of nitrate, nitrite, and nitro groups in organic material with the use of atomic absorption spectrophotometry (AAS) has been described by Houser & Fauth (1).

The AAS method is based on the formation of a copper neocuproine nitrate complex, which is then extracted with methyl isobutyl ketone (MIBK). The amount of complexed copper is determined by AAS, and it is directly proportional to the nitrate content. Nitro and nitrite groups can also be selectively determined by selective reduction or oxidation in the presence of nitrate ions. The aim of this work is to present a case of accidental occupational intoxication and the application

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of the method described by Houser & Fauth (1) to prove that the accident was probably caused by the improper handling of concentrated nitric acid.

Case description

A 48-year-old dairy worker was working alone in the evening (1800–2000) in a room where whey and milk powders are mixed in a large mixer. Workers in adjacent workrooms suddenly experienced what they described as a distinct “acid smell.” The worker in question, when asked later about what had happened, replied that he had “just been splashing about a little.” During the following night he complained of loss of breath and tightness in his chest. He was then taken to the hospital with a developing pulmonary

edema and immediately placed in a respirator.

As the worker could not be questioned, the local occupational safety personnel attempted to reconstruct the accident and proposed the following course for it: The worker had been washing some equipment and was cleaning up in the room when, suddenly, the floor drain became clogged with whey and milk powder. It was not possible to flush away the obstruction with water, so he made an attempt to dissolve it with concentrated nitric acid, which was available in an adjacent room. The reaction between the acid, water, and whey and milk powder was probably violent, large amounts of nitrogen oxides evolving, which he continued to inhale for several minutes before the air cleared. Since the worker was not following the normal instructions for this kind of work, it is likely that he was deliberately vague when he referred to the incident as “just ... splashing about a little.”

This theory was confirmed by several findings in the room after the accident. The iron gratings in the floor drain were very corroded; the covering on the walls and powder mixers, previously white, had become yellowish; paper sacks in the room during the accident had become very brittle.

The samples, described in table 1, were collected and sent to our laboratory for analysis in an attempt to verify the hypothesis.

Materials and methods

Materials and reagents. All reagents used were of pro analysi or higher quality. Water was purified in a Millipore R/Q

Table 1. Description of the samples.

Sample	Origin
1	Pure whey powder
2	Pure milk powder
3	New paper sack
4	Yellowish wall covering
5	Yellowish covering from the powder mixers
6	Brittle paper sack

Table 2. Results of the pH measurements.

Sample	pH	N
Water blank	7.0	2
3	6.2	3
6	3.0	3

Table 3. Determination of nitrogen oxides.

Sample	Nitrate ($\mu\text{g}/\text{mg}$)	Nitro groups ($\mu\text{g}/\text{mg}$)	Total nitrogen oxides ^a ($\mu\text{g}/\text{mg}$)	N
1	nd ^b	nd	nd	1
2	nd	nd	nd	1
3	nd	nd	nd	2
4	1.8	nd	1.8	2
5	2.6	nd	2.6	2
6	1.0	nd	1.0	3

^a As nitrates.

^b Practical limit of detection 0.2 $\mu\text{g}/\text{mg}$ (nd = not detected).

water purifier; and all glassware was washed with detergent and tap water, soaked in nitric acid, and then rinsed several times in deionized water.

With the method for the indirect determination of nitrogen oxides by AAS (1) the following reagents were used: copper (II) sulfate (0.01 M), hydroxylammonium sulfate (5 % w/v), ammonium dihydrogen phosphate (0.5 M), neocuproine in MIBK (0.002 M), cerium (IV) sulfate (0.1 N in 10 % sulfuric acid), sulfamic acid (2 % w/v in 10 % sulfuric acid), and potassium permanganate (0.1 N in 10 % sulfuric acid). As nitrate stock solution, a commercial silver nitrate AAS standard solution was used (British Dirty House, 1,000 $\mu\text{g/ml}$, 575 $\mu\text{g/ml}$ referring to nitrate).

The pH measurements were carried out with a Radiometer PHM 63 digital pH meter, and the atomic absorption determinations with a PYE Unicam SP 1900 atomic absorption spectrophotometer with a copper hollow-cathode lamp at 324.7 nm. Pure MIBK was used as the blank rather than a neocuproine-MIBK solution in order to eliminate errors due to the evaporation of MIBK and a subsequent concentration of the solution. Correction for the reagent blank was made when necessary.

pH measurements. Approximately 150-mg samples from the paper sacks were weighed in 50-ml beakers. The samples were leached in 20 ml of water for 1 h, and the pH of the water extracts was determined.

AAS determinations. Samples from the powders, 15–30 mg, were suspended in 5 ml of water, and samples from the paper sacks were leached as previously described. Appropriate standard solutions were made by diluting the nitrate stock solution. To two series of 20- to 25-ml stoppered flasks 1-ml portions of the samples, suspensions and extracts, or standards were added. To the first series, 1 ml of water was added, and to the second 1 ml of cerium sulfate or potassium permanganate, in order to oxidize the nitro and nitrite groups to nitrate. Then 1 ml of copper sulfate solution, 1 ml of hydroxylammonium sulfate solution, and 5 ml of ammonium dihydrogen phosphate solution were added to both

series, and the flasks were swirled to mix the contents. Then 10 ml of neocuproine in MIBK was pipetted into each flask, and the flasks were thoroughly shaken for at least 2 min before the layers were allowed to separate. The copper content in the organic layer, which is proportional to the nitrate content, was determined by atomic absorption analysis. The results from the first series gave the nitrate content of the sample, and from the second series the total amount of nitrogen oxides in the samples was determined.

Results and discussion

The pH measurements (table 2) showed that the samples from the contaminated paper sacks gave aqueous extracts with a pH lower than that of the pure paper sacks. The results indicate that the paper sacks, which were found to be brittle, had been contaminated by acid.

Table 3 shows the results from the determination of nitrogen oxides. As can be seen, nitrates were found only in the samples collected in the room after the accident. The use of cerium sulfate or potassium permanganate for the oxidation of nitrite and nitro groups to nitrates did not show any difference in the total amount of nitrogen oxides in the samples.

The results — low pH and high nitrate content — and the observations in the room after the accident — the corrosion of the floor drain, discoloration of the wall covering, and brittleness of the paper sacks — strongly support the hypothesis proposed for the course of the accident. It is, however, not possible to draw any conclusions on the basis of these results about the atmospheric concentration of the nitrogen oxides to which the injured worker was exposed.

This work shows that an analytical problem in occupational medicine can sometimes be solved by the application of an analytical method originally meant for a totally different purpose.

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