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OCCURRENCE OF HYDROCYANIC ACID IN THE PROCESS OF BRIQUETTING OF FERROSILICON AND RHODANATE CONCENTRATIONS IN THE URINE OF EXPOSED WORKERS

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ABSTRACT

The presence of hydrocyanic acid (HCN) in the atmosphere of the working premises during the technological process of briquetting of ferrosilicon was detected, a fact that had hitherto been unknown. The presence of HCN had not even been suspected, since this acid neither occurs in the basic raw material, nor during the briquetting process. In the course of the initial examinations of the atmosphere of the working premises, the values for HCN went up to 30 ppm. After the technical protection measures were taken, the concentrations of HCN varied from 0.5 to 5.0 ppm, depending on the workplace, the type and the intensity of work.

In order to establish the effectiveness of the protection measures at the place of work, the effect of exposure upon workers' health and the timely prevention of noxious effects, health examinations of the workers were made at intervals of three to five months. During a two-year survey different values of thiocyanates in the urine of exposed workers were found, but these did not exceed the values found in non-exposed persons who were smokers (up to 9 mg/l urine). The average values of thiocyanates in exposed persons were between 3.5–6.3 mg/l. The values of thiocyanates in the urine of exposed persons measured before and after eight hours of work were higher after work, but within the limits of the values found in non-exposed smokers. In our group of non-exposed non-smokers rhodanate concentrations were higher than those reported in the literature.

During the technological process of the briquetting of ferrosilicon the presence of hydrogen cyanide was detected in the working environment in concentrations which exceeded the maximum permissible levels and caused acute intoxication of a group of workers[1]. Since the possibility of the presence of cyanide compounds had never occurred earlier, the safety measures were not adequate. After the safety measures were introduced, their effect on both the concentration of these compounds in the working environment, where HCN concentration has decreased but is still present, and on the health of the exposed workers has been studied.

The aim of this study was to point at the occurrence of toxic substances in the atmosphere of the working premises which are not expected considering the

composition of the raw materials and the type of technological process, even when the process is non-hermetic.

SUBJECTS AND METHODS

The working conditions were assessed by the standard procedure used in occupational medicine. The HCN concentrations in the working environment were simultaneously measured by Dräger indicator tubes and the argentometric method after Liebeg[4].

The values of HCN in air were compared to the permissible concentrations according to the Yugoslav standards[5]. They amounted to 0.27 ppm or 0.3 mg per m^3 of air.

A medical check-up of exposed workers was conducted in three- and five--month intervals. The examination covered 18 workers employed at workplaces where the presence of cyanide compounds was proved.

In the urine of the exposed workers thiocyanate ions (rhodanate) were determined by the method of Densen and co-workers[2]. The determination of rhodanate in urine was also performed in 95 control subjects grouped according to smoking habit into: Group 1:51 non-smokers; Group 2:32 moderate smokers (up to 25 cigarettes a day); and Group 3:12 heavy smokers (over 25 cigarettes a day).

The briquetting of ferrosilicon (grinding, sieving, sacking, feeding into the mixer and mixing with water glass, pressing and storing) was carried out in a primitive way. The sieving of the ground mass was done by hand on wire screens in the open, not protected from wind and other atmospheric influences. The ground material was not left to stand but was used immediately. The mixing of the mass, pressing, storing and packing were carried out in one room without artificial aeration.

After the safety measures had been introduced, the system of grinding and sieving partly became airtight, the ground material was left to stand, the mixer was placed in a separate room with built-in drain ventilation, pressed briquettes were carried to a separate room, and the workers took frequent breaks during the working hours.

RESULTS AND DISCUSSION

Table 1 illustrates the concentrations of hydrogen cyanide in the working environment in different time intervals before and after introduction of the safety measures. HCN concentrations in the working environment before the safety measures were introduced had ranged from 15 ppm above stored briquettes to 25 and 30 ppm during the mixing of the ground ferrosilicon. After the safety measures had been introduced (longer standing of the ground material, better aeration and isolation of different phases of the process of work) HCN concentrations were considerably smaller in the same working operations and varied from 0.5 to 5 ppm. Yet, all measured concentrations exceeded the maximum permissible values for HCN. Above the non-ground material HCN

TABLE 1
HCN concentration determined by indicator tubes (ppm) in the working environment before and after introduction of the safety measures.

Place of testing	Before introduction of the safety measures	After introduction of the safety measures	
	March 1975	June 1975	September 1977
Grinding	20–25	4	3–5
Sieving	20–25	5.5	2–3
Mixing	25–30	4	3–4
Pressing	15–20	5	0.5–2
Storing	15	4.8	0.5
Above raw material	0.75	0.5	in traces

values ranged from 0.75 ppm in the first testing to "trace amounts" indicating varying HCN amounts in the raw material, depending upon weather conditions.

During the sieving of the ground mass HCN concentrations reached the values of 20 and 25 ppm, but a short time after the material had been left to stand the values decreased to 1–2 ppm. During the feeding of the ground and screened material into the mixer before the safety measures were introduced HCN values had increased to 25 ppm again but only for a short time. As soon as the binding agent was added (water glass or similar) the values decreased to 4 ppm. After the material had been left to stand, HCN levels increased only to 5 ppm during the phase of feeding and mixing.

After introduction of safety measures these values dropped considerably (5, 1, 4–5 and 1 ppm). The results of the testing of HCN concentrations in the working environment simultaneously by the indicator tubes and argentometric method are shown in Table 2. The values obtained by the argentometric method are a little higher than those obtained by the indicator tubes the chemical method for the quantification of gases being more sensitive.

No objective changes in the health of the exposed workers were observed after strict precautionary measures had been introduced. The complaints

TABLE 2
HCN concentrations in the working environment obtained by the indicator tubes and argentometric method.

Place of testing	HCN concentrations (Sept. 1975)		
	Indicator tubes	Argentometric method	
	ppm	ppm	mg/m³
Grinding	2.5	3.15	3.8
Sieving	3	5.06	6.1
Mixing	3	3.36	4.1
Pressing (briquetting)	3	4.23	5.1
Storing	2	4.15	5.0

pertaining to subjective troubles existing before the introduction of the safety measures diminished as well.

Rhodanate concentrations in urine before and after work for the group of workers engaged in the briquetting of ferrosilicion in different working operations are shown in Table 3 for the tests performed in 1976. The average calculated values of rhodanate concentrations in the urine in our workers who

TABLE 3
Rhodanate concentrations in urine (mg/l) before and after work in the group of exposed workers in different operations of work. (The results of the testing in 1976.)

Working operation	No. of subjects	Rhodanate concentration in mg/l			
		Smokers			
		Before work		After work	
		$\bar{X}$	Range	$\bar{X}$	Range
Grinding and sieving	4	4.25	2.0–7.0	3.75	1.5–6.5
Mixing	5	6.12	3.5–7.5	6.43	5.5–7.0
Pressing	9	4.55	1.5–9.0	6.12	3.0–9.0
Total	18	4.43	1.5–9.0	5.39	1.5–9.0

were smokers were within the limit values normally found in smokers (9.0 mg per litre). However, the testing of these values before and after work showed a statistically significant increase after work ($t = 2.742$, $p < 0.05$). Similar values were obtained in measurements conducted in April 1978. During the mixing and

TABLE 4
Rhodanate concentrations in urine (mg/l) in the exposed workers in 1975 and 1978.

Type of the operation	Year of testing	No. of subjects	Length of exposure (years) $\bar{X}$	Rhodanate concentration in urine (mg/l)	
				$\bar{X}$	Range
Grinding	1975	5	2.5	3.60	2.0–5.0
Mixing		5	2	4.92	2.5–7.0
Pressing		9	1.5	5.25	1.8–9.0
Total		19	2	4.59*	1.8–9.0
Grinding	1978	5	5.4	7.96	4.6–10.6
Mixing		5	5.6	6.96	4.8–11.0
Pressing		9	3.7	7.98	4.0–18.5
Total		19	4.9	7.63*	4.0–18.5

*$t = 18.6$, $p < 0.001$

sieving of the mass the differences in the values were more evident. Rhodanate concentrations obtained in the tests carried out in 1975 and 1978 in the same workers were compared. A statistically highly significant increase of the mean values of rhodanate in urine was observed with an increased length of exposure. In 1975 : $\overline{X}_1 = 4.59$ mg/l and in 1978 : 7.63 mg/l ($p < 0.001$). In the group of 5 non-exposed workers the rhodanate concentration in 1975 was 4.87 mg/l and in 1978 4.45 mg/l.

Table 5 shows the rhodanate levels in the urine of the control group of non-exposed individuals. By testing rhodanate concentrations in the urine of subjects not exposed to cyanide compounds the authors found the mean concentrations of 2.85 mg/l in non-smokers, which are higher than those regarded as standard[7] and accepted by some investigators[3,6] (for non-smokers 0, for occasional smokers 1.2 mg/l). The values observed in our group of smokers were within the above limits.

TABLE 5

Rhodanate concentrations (mean ± S.D.) in urine (mg/l) in non-exposed persons according to smoking habit.

Group of subjects		No. of subjects	Rhodanate concentration		Variance	Coefficient of variation (CV %)
Non-smokers		51	2.85	± 1.23	1.5	43.0
Smokers	< 25 cigarretes	32	6.00	± 1.78	3.2	16.7
	> 25 cigarretes	12	7.50	± 1.55	2.4	32.0

Non-smokers : smokers (< 25 cigarettes) — $p < 0.001$

On the basis of the results of this study it appears that the determination of rhodanate concentrations as a test of exposure to small doses of cyanide is useful only for testing the exposure of the group or for longitudinal follow-up of rhodanate concentrations in individuals, whereas single rhodanate concentrations are of little use. A diversity of obtained results in our subjects, in whom single concentrations reached the value of 11 mg per litre urine in non-exposed non-smokers and only 1 mg/l in individual smokers exposed to cyanides, supports our conclusion.

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