

Determination of ethylene oxide and ethylene chlorohydrin in red pepper

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Mainly gaseous ethylene oxide is used on a technical scale for the sterilization of dried vegetables and spices. Some of the ethylene oxide is adsorbed on the surface of the dried product, while part of it is converted chemically to ethylene chlorohydrin, to the 1,2-diol to its esters and to hydroxyethylamine derivatives.

The ethylene chlorohydrin formed from ethylene oxide was first determined in red pepper in 1976 by STIJVE, KALSBACH and EYRING /1/, who used a gas-chromatographic and layer-chromatographic method. In contrast with the earlier assumptions, they demonstrated that ethylene oxide does not give rise to the formation of ethylene bromohydrin in dried products; only ethylene chlorohydrin is present.

Their procedure for determination of the adsorptively-bound ethylene oxide residue is not a clear-cut one /2,3/. In 1978, PFEILSTICKER and LEYENDECKER /4/ reported a spectrophotometric procedure for the analysis of ethylene chlorohydrin in the presence of ethylene oxide, in the homogeneous phase, in chocolate drinks and cocoa drinks.

We have developed a procedure for the determination of ethylene chlorohydrin, and of ethylene chlorohydrin in the presence of ethylene oxide, in the heterogeneous phase, i.e. in an aqueous suspension of red pepper. The essence of the procedure: the ethylene oxide adsorbed to the red pepper, and the ethylene chlorohydrin formed from the ethylene oxide, are hydrolyzed to glycol with sulphuric acid solution in an aqueous suspension of the pepper, and the glycol in the aqueous pepper suspension is oxidized with sodium meta periodate solution to formaldehyde. The red pepper is filtered out from the aqueous solution of formaldehyde, and the formaldehyde is distilled from the filtrate into an aqueous sulphuric acid solution of chromotropic acid. The concentration of the blue colour produced is determined by spectrophotometric measurement at 570 nm, with reference to the concentrations of standard solutions. This procedure gives the combined amounts of ethylene oxide and ethylene chlorohydrin in the red pepper. It is generally sufficient to express the quantity of ethylene oxide and ethylene chlorohydrin as metabolized "ethylene chlorohydrin", the limiting value of which in the case of red pepper is 300 mg/kg. In some countries, including The Netherlands and Belgium, a limiting value is also given for the amount of ethylene oxide /1/. For technological, economic, hygienic and toxicological reasons, the "free" ethylene oxide content in milled red pepper may be necessary too. Our procedure will satisfy this requirement as well from an aqueous extract of the red pepper, the "free" ethylene oxide is distilled off at the original pH of the suspension and is hydrolyzed with aqueous sulphuric acid; the glycol formed is oxidized as above to formaldehyde, which is converted with chromotropic acid to a blue colour equivalent to the ethylene oxide, which can be measured colorimetrically. The procedure elaborated for the determination of the ethylene oxide and ethylene chlorohydrin contents of red pepper therefore consists of methods "A" and "B". Method "A" involves the joint determination of ethylene oxide and ethylene chlorohydrin, while method "B" involves the determination of ethylene oxide in the presence of ethylene chlorohydrin. The quantity of metabolized ethylene chlorohydrin formed from ethylene oxide in red pepper is given by the difference of the results of methods "A" and "B".

The determinations of ethylene oxide and ethylene chlorohydrin via formaldehyde are sensitive ones: it is possible to detect ethylene oxide and ethylene chlorohydrin in quantities of 10-20 mg/kg.

Course of the analysisMethod "A"

10 g milled red pepper is suspended in 50 cm³ distilled water at 4°C in a 250 cm³ round-bottomed flask, and 5 cm³ 2 N sodium hydroxide solution is added to the suspension during stirring. The flask is cooled in ice-water, and the pH of the aqueous suspension is adjusted to a value of 2 with 0,1 N sulphuric acid solution during the cooling. At this pH value the glycol formed is oxidized with 40 cm³ 0,05 M sodium metaperiodate. The oxidation is made complete by refluxing the suspension on a water-bath for 10 minutes, and the flask is then cooled with a stream of water to room temperature. The aqueous suspension is filtered through a fluted filter into a 250 cm³ round-bottomed flask, and the flask and the filter paper are carefully washed with distilled water. About 45 cm³ liquid is distilled from the filtrate into a 50 cm³ volumetric flask cooled with an ice-salt mixture. The cooling-water in the condenser should be at a temperature of less than 15°C, and the joints in the apparatus should be well sealed with silicone grease. The liquid in the volumetric flask is made up to 50 cm³ with distilled water at 20°C. The distillate contains formaldehyde equivalent to the ethylene chlorohydrin plus ethylene oxide initially present in the pepper. A 1 cm³ aliquot of the distillate is transferred to a 25 cm³ Erlenmeyer flask already containing 1 cm³ 0,5 % chromotropic acid solution. In small portions, 8 cm³ 81 % sulphuric

As seen from the results presented in Table 2, high variations in the examined metal contents were established in analyzed samples of nitrites and nitrates. In addition, it can be stated that nitrites contain higher cadmium, copper, arsenic and lead quantities than nitrates. All analyzed samples of nitrites and nitrates showed lower copper and lead contents than the limits prescribed by EEC (37). It is important to emphasize that 63.33% of nitrite samples and 86.66% of nitrate ones had less than 3 mg/kg of arsenic.

We consider, with regard to a great matrix effect specially in the case of sodium chloride, that it is necessary for the examined additives simultaneously with issuing rules on the limit quantities of toxic metals, although most modern techniques are used, to define precisely their content determination methodology and the method sensitivity limit. Our examination results show that it is desirable, regardless of the applied methodology, to employ the standard addition procedure as well as that both flame and flameless photometry can be applied in the lead, cadmium and copper content determination.

References

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Comparative determination results of lead, cadmium and copper contents in Na_2HPO_4 , NaCl , NaNO_2 and NaNO_3 , by FS and CRA methods

Table 1.

	L e a d					C a d m i u m					C o p p e r				
	F S			C R A		F S			C R A		F S			C R A	
	C	F	R	F	R	C	F	R	F	R	C	F	R	F	R
NaCl	5.36	5.71	103.74	5.17	95.38	1.12	1.12	90.32	1.15	97.69	5.12	4.42	88.49	4.87	95.97
	7.36	6.75	98.66	6.95	92.35	2.12	2.20	92.18	2.04	95.24	10.12	8.93	90.37	9.76	97.28
	10.36	10.34	106.49	9.83	93.89	3.12	3.01	91.76	3.13	97.12	15.12	13.70	91.59	14.65	96.80
NaNO_2	5.23	4.61	88.73	5.04	94.91	1.07	1.07	92.20	1.07	93.70	5.17	4.78	88.43	4.78	90.34
	7.23	5.98	85.24	6.75	91.35	2.07	1.96	89.49	1.89	90.54	10.17	9.13	87.19	9.53	92.36
	10.23	9.03	90.56	9.87	95.31	3.07	2.88	89.26	2.93	94.08	15.17	13.75	89.36	14.09	92.10
NaNO_3	5.28	4.79	92.89	4.99	95.57	1.14	0.98	93.26	1.10	101.34	5.09	4.71	91.79	4.75	94.38
	7.28	6.80	95.96	7.00	96.48	2.14	2.05	97.48	2.15	99.56	10.09	9.19	90.37	9.31	92.01
	10.28	9.63	96.12	9.77	95.02	3.14	2.95	96.87	3.18	100.22	15.09	13.93	92.24	14.18	93.67
Na_2HPO_4	10.32	8.87	90.14	9.47	93.84	1.17	0.99	90.87	1.24	98.58	5.30	4.60	90.93	5.08	98.19
	15.32	14.03	93.05	14.26	94.06	2.17	1.92	90.14	2.18	97.62	10.30	8.97	88.75	10.44	102.82
	20.32	17.95	88.93	19.85	98.37	3.17	3.12	95.71	3.08	96.26	15.30	13.41	89.23	15.10	99.07

C - Element calculated quantity - based on the quantity in the sample as well as the added quantity, mg/kg

F - Established element quantity, mg/kg

R - Recovery, %

FS - Flame spectroscopy

CRA - Carbon rod atomizer

Analysis results of polyphosphates, sodiumchloride, nitrites and nitrates*

Table 2.

		L e a d		C a d m i u m		C o p p e r		A r s e n i c		M e r c u r y	
P o l y p h o s p h a t e s	N = 80	\bar{x}	9.26	3.68	7.22	2.30	1.56				
		range	3.47-15.62	1.89-5.47	1.25-23.20	1.54-3.30	0.46-4.06				
		s	2.61	1.21	7.24	0.46	0.86				
		C_v	28.19	32.84	100.23	20.11	55.22				
S o d i u m c h l o r i d e	N = 60	\bar{x}	3.94	1.45	2.41	1.87	0.53				
		range	1.82-7.85	0.41-5.36	1.26-3.42	0.82-3.17	0.02-1.41				
		s	1.63	1.12	0.55	0.75	0.36				
		C_v	41.13	76.85	22.76	40.17	67.15				
N i t r i t e s	N = 40	\bar{x}	5.20	1.32	4.15	2.80	0.36				
		range	3.58-7.05	0.22-2.38	1.22-6.36	1.37-4.53	0.21-0.70				
		s	0.94	0.77	1.49	0.92	0.13				
		C_v	18.07	58.49	35.93	32.91	35.85				
N i t r a t e s	N = 40	\bar{x}	3.98	0.87	2.73	2.14	0.53				
		range	2.48-6.52	0.42-1.68	1.75-3.94	1.03-3.42	0.00-1.02				
		s	1.17	0.29	0.57	0.72	0.27				
		C_v	29.24	33.00	20.94	33.59	51.18				

N - Analyzed samples number

s - Standard deviation

\bar{x} - Mean value

C_v - Variation coefficient

* element quantity in mg/kg