Reducing Phosphine after the Smoking Process Using an Oxidative Treatment

Giorgio Nota,* Daniele Naviglio, Raffaele Romano, Maurizio Ugliano, and Valentina Sabia

Dipartimento di Scienza degli Alimenti, Università degli Studi di Napoli "Federico II", Via Università 100, 80055 Portici, Napoli, Italy

This article gives a description of the setup in a laboratory of a pilot system to reduce phosphine following the smoking process of foodstuffs. At present, this fumigant is released into the atmosphere and causes serious damage to the environment due to its transformation into aggressive compounds. However, phosphine may prove a good alternative to methyl bromide, which will legally be used as a fumigant until the year 2002, provided it is made inert after the smoking process and transformed into nontoxic and easily disposable substances. Oxidant solutions containing potassium permanganate or potassium bichromate in suitable concentrations proved moderately effective in reducing phosphine. The addition of traces of silver nitrate as a catalyst to the oxidant solutions increased the efficiency in reducing the fumigant, although not completely. Thus it was necessary to use a recycling system to decontaminate air from phosphine, as such an apparatus ensures the complete reduction of phosphine. The mathematical function describing how the concentration of phosphine varies in the smoking chamber also makes it possible to estimate the time necessary to reduce a phosphine concentration from any initial value to a fixed final value.

Keywords: *Bichromate; foodstuffs; fumigation; oxidation; permanganate; phosphine; smoking*

INTRODUCTION

The smoking process is a very common industrial practice, especially for the conservation of foodstuffs. The most commonly used fumigants are methyl bromide and phosphine. The use of methyl bromide will only be permitted worldwide for the first 10 years of the new millennium as provided for by the 1995 Montreal Treaty, whereas in the United States its use will be permitted until the year 2001 (Noling and Becker, 1994). Consequently, a wider use of phosphine is to be expected. Following the smoking process, the leftover phosphine is often freely released into the atmosphere, causing serious damage to the environment (Glindemann et al., 1996). The scope of the present article is to set up a laboratory procedure to inactivate phosphine following the smoking process.

Phosphine is a poorly water-soluble gas (1.7 mg/L) at room temperature and has strong reducing properties (Halmann, 1972). It was decided to take a sample of phosphine containing air from a container simulating a smoking chamber and to make it bubble in an oxidizing solution, to transform phosphine into phosphate, a nonvolatile substance. Since phosphine is poorly soluble in water, it is necessary to find an oxidant which is sufficiently fast kinetically so that phosphine oxidizes quickly during contact with the oxidizing solution. To avoid any possibility of phosphine bypassing the oxidative process and being released into the atmosphere, the air to be purified is sent through the smoking chamber a second time, and this recycling process is repeated until the concentration of phosphine reaches the level desired.

* To whom correspondence should be addressed. Phone: 0039 0817755168. Fax: 0039 0817755345. E-mail: nota@cds.unina.it.

MATERIALS AND METHODS

Chemicals. Potassium permanganate, potassium bichromate, and silver nitrate were purchased from Fluka Chemie (Buchs, Switzerland), and all were of analytical grade; the cylinder containing phosphine (2170 ppmv) in nitrogen was purchased from SOL SpA (Caserta, Italy). The apparatus for measuring the efficiency of the reduction of phosphine and the recycling system for the reduction process were created in our laboratory.

Choice of Oxidant. During the oxidative process, phosphine may vary its oxidation number from -3 to $+5$, losing up to 8 electrons. Bearing this in mind, oxidants with a wide variation in oxidation number were used, and for financial reasons low-cost oxidants were chosen. After preliminary tests on various oxidants, potassium permanganate and potassium dichromate were chosen. Given the oxidative and catalytic properties of silver ions, silver nitrate was also considered.

Oxidation with Potassium Permanganate ($KMnO_4$). In neutral media, the reduction of permanganate results in the production of manganese dioxide, which precipitates. However in acidic media the reduction product is the manganese ion Mn^{2+}, which remains in solution. Despite the higher costs incurred, we chose to use an acidic environment because of the greater variation in the oxidation number and the soluble compounds obtained, which are more easily disposable. In our experiment, we used a 0.2 M solution of $KMnO_4$ in the presence of H_2SO_4 (2 N).

Oxidation with Potassium Dichromate ($K_2Cr_2O_7$). In acidic media, the reduction product of $Cr_2O_7^{2-}$ ion is composed only of Cr^{3+}, which remains in solution and is therefore easily disposable. The experiment was conducted with 0.2 M $Cr_2O_7^{2-}$ solution in the presence of H_2SO_4 (2 N).

Oxidation with Silver Nitrate. The reduction product of silver ions is the metalline silver. The possibility of using this oxidant was verified with a 0.01 N solution of $AgNO_3$.

Apparatus To Test the Efficiency in Reducing Phosphine by Oxidizing Solutions. To test the efficiency of the above-mentioned oxidants, the following procedure and the apparatus described in Figure 1 were used.

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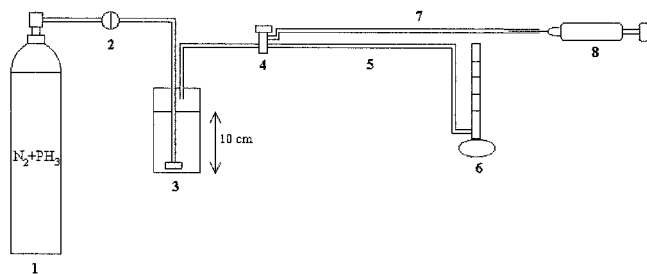*J. Agric. Food Chem.,* Vol. 48, No. 2, 2000 **521**

Figure 1. Flowchart to test the efficiency of the oxidant solution for the reduction of phosphine. Legend: (1) cylinder containing the phosphine−nitrogen mixture (3.1 g/m³); (2) needle valve for regulation of the flow (Φ); (3) impinger containing porous septum; (4) flow deviator; (5) line; (6) bubble flow-meter; (7) line; (8) gastight syringe for sampling gas.
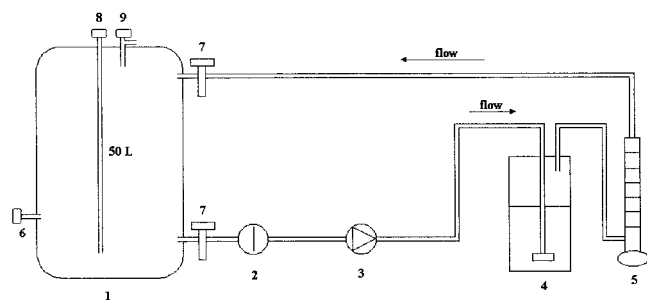

Figure 2. Recycle system for the reduction of phosphine. Legend: (1) 50-L polyethylene container; (2) needle valve for regulation of the flow (Φ); (3) pump; (4) impinger containing oxidant; (5) bubble flow-meter; (6) hole for phosphine sampling; (7) on−off faucets; (8) hole for filling the container; (9) hole for vent.

Procedure. After being prepared as described above, 200 mL of the oxidant solution to be tested was placed inside the impinger (3). Under our experimental conditions, the head of the liquid used was 10 cm; the valve (4) was turned to the line (5); a solution at a known concentration of phosphine in nitrogen was passed through the oxidant solution; the flow was regulated by adjusting the needle valve (2) and measured with the soap bubble flow-meter (6); the valve (4) was turned to the measurement line (7); the gas mixture of phosphine−nitrogen was made to flow in line (7) for 1 min in order to equilibrate and saturate the line with the gas; the gas was sampled by means of a gastight syringe (8); and the phosphine concentration was measured by means of gas chromatography (Brunner et al., 1995). The procedure was carried out for flows ranging from 20 to 90 L/h.

Efficiency Calculation. The oxidative efficiency of the tested solutions was calculated as

$$E_{ox}\,(\%) = \frac{(C_1 - C_2)}{C_1} \times 100 \qquad (1)$$

where C_1 is the concentration of phosphine at the entrance point of the oxidizing solution and C_2 is the concentration of phosphine at the exit point of the oxidizing solution.

Recycle System for the Reduction of Phosphine. Figure 2 reports the flowchart of the apparatus used to simulate the reduction of phosphine in a smoking chamber.

Procedure. The impinger (4) was filled with 200 mL of oxidizing solution; the faucets (8 and 9) were closed; the faucets (7) were opened; the pump (3) was turned on, and the flow was regulated using the needle valve (2); the flow was measured using the soap bubble flow-meter (5) and the chronometer; the pump was turned off, and the faucets (7) were closed; the vent (9) was opened; a mixture of 2170 ppmv phosphine in nitrogen coming from a gas cylinder was sent through opening 8 to the 50-L capacity polyethylene container (1); by trial and error, a known titer concentration of phos-

Table 1. Reducing Efficiency (%) of Phosphine by KMnO₄ (0.2 M) Solutions with and without Adding AgNO₃ Depending on Flow Variation

		KMnO₄ (0.2 M) + AgNO₃			
flow (L/h)	KMnO₄ (0.2 M)	AgNO₃ (0.01 M)	AgNO₃ (0.005 M)	AgNO₃ (0.001 M)	AgNO₃ (0.0001 M)
20	85	98	97	94	90
50	60	89	89	81	73
90	13	60	51	43	30

Table 2. Reducing Efficiency (%) of Phosphine by K₂Cr₂O₇ (0.2 M) Solutions with and without Adding AgNO₃ Depending on Flow Variation

		K₂Cr₂O₇ (0.2 M) + AgNO₃			
flow (L/h)	K₂Cr₂O₇ (0.2 M)	AgNO₃ (0.01 M)	AgNO₃ (0.005 M)	AgNO₃ (0.001 M)	AgNO₃ (0.0001 M)
20	90	99	97	93	90
50	65	93	85	84	72
90	20	64	56	40	30

phine, i.e., between 400 and 700 ppmv, was produced inside the plastic container; the faucets (8 and 9) were closed, and the faucets (7) were opened; the pump was turned on; the gas was sampled by means of a gastight syringe introduced into hole 6; and the phosphine concentration was measured by means of gas chromatography. Last, the data obtained concerning the phosphine concentration in the simulated smoking chamber (container 1) were graphically reported over time.

RESULTS AND DISCUSSION

Efficiency of the Oxidation of Phosphine with Permanganate and Potassium Dichromate. The system illustrated in Figure 1 allows a calculation to be made of the efficiency of the oxidizing solutions in reducing phosphine levels. Under our experimental conditions, the tests conducted using KMnO₄ in the presence of sulfuric acid proved that part of the phosphine concentration was able to bypass the oxidative process, even when the flow of air to be purified was reduced. Moreover, despite the acidic media, a brown solid, which turned out to be MnO₂, surprisingly formed during the reaction. This should be avoided since a solid phase creates problems with the bubbling process as well as difficulties when cleaning the impinger.

Tests using potassium dichromate in acidic media also showed that the reduction yield did not reach 100%, even at low flow levels. Unlike permanganate, however, there was no evidence that a solid phase formed. The partial oxidative yield of these oxidants can be attributed to kinetic factors and not to unfavorable thermodynamic conditions. The results of the reduction tests using permanganate and dichromate are reported by flow rate between 20 and 90 L/h, in Tables 1 and 2, respectively.

Efficiency of the Oxidation of Phosphine by Silver Nitrate. Silver ions have a relatively high reduction potential and fast kinetics, which make it useful as a catalyst in redox reactions (its use is important in determining the chemical oxygen demand (C.O.D.)) (AOAC, 1995). Fortunately, this was also the case when using silver for the oxidation of phosphine. Using a 0.01 N solution of silver nitrate, flows between 20 and 50 L/h gave an oxidative yield of 100% which was not significantly reduced for much higher flows. The evaluation of the results of phosphine reduction suggests that silver nitrate completely blocks phosphine, even at reasonably high flows. However, the elevated cost of this oxidant makes its use prohibitive in practical

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applications, although it may be used as a catalyst in tandem with permanganate or dichromate, which are much cheaper oxidants.

Oxidation of Phosphine Using Permanganate or Dichromate in the Presence of Silver Ions as Catalyst. To reduce costs and retain a high efficiency of phosphine reduction, the silver ion was tested as a catalyst. For this purpose, different solutions of permanganate with concentrations of silver ions between 0.01 and 0.0001 N were prepared. The oxidative efficiency of these solutions was determined for a mixture of phosphine in nitrogen (2170 ppmv), and the flow was regulated to between 20 and 90 L/h. The results, which are reported in Table 1, indicate that the oxidative efficiency of permanganate solutions in the presence of Ag$^+$ is always higher than that of solutions in the absence of Ag$^+$. However, permanganate solutions show a remarkable variation in efficiency versus the flow, and this varies from 85% to 13% for a flow change of between 20 and 90 L/h. The addition of Ag$^+$ to permanganate solutions makes the efficiency less variable depending on the flow, and even 0.0001 N concentrations in Ag$^+$ show this phenomenon.

To verify that the oxidative efficiency was not due solely to the presence of the silver ion, a quantity of phosphine 20 times greater than the stoichiometric quantity was passed through the oxidizing solutions. In this case, its efficiency also remained constant. This may be explained by the fact that, in solution, the silver ion oxidizes phosphine. A finely dispersed metalline silver results from this process, and it is rapidly oxidized by permanganate to silver ion, which returns to the cycle.

Unfortunately, as occurs when Ag$^+$ is absent, a small quantity of manganese dioxide forms during the oxidation process as a result of the oxidation of a part of the phosphine by the permanganate. In the same way, solutions of dichromate were prepared using equal concentrations of Ag$^+$ which had already been used for permanganate solutions. The oxidative efficiency of these solutions was determined in the same way for a mixture of phosphine in nitrogen (2170 ppmv), and the flow was regulated to between 20 and 90 L/h. The results, which are reported in Table 2, indicate that even with dichromate, the oxidative efficiency of solutions containing silver ions was always higher than that of solutions where Ag$^+$ was absent. Thus, the same comments about permanganate solutions are still valid. Again in this case, the silver ion oxidizes the phosphine in solution, the metalline silver which forms is oxidized by the dichromate, and the silver ion returns to the cycle. During the process, there was no evidence that any solid residue was formed. It may therefore be concluded from the above that permanganate and dichromate have the same oxidizing behavior.

Study of the Parameters That Affect the Time Required for the Reduction of Phosphine in a Smoking Chamber Utilizing a Recycling System. Figure 3 reports the way in which the concentration of phosphine varies over time in the smoking chamber when using a recycling system. As an oxidizing mixture, a solution of dichromate containing a proper concentration of Ag$^+$ as a catalyst was used. The points reported in Figure 3 represent experimental values; these points are described in an exponential equation of the type

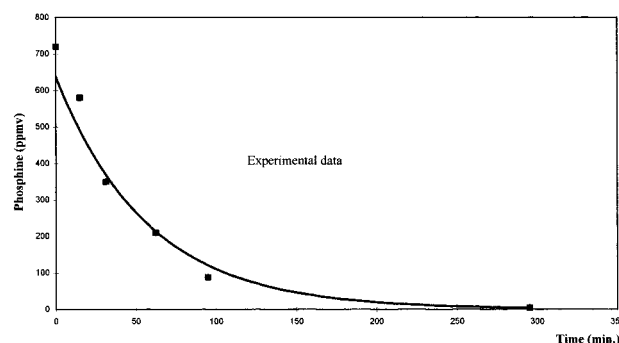$$y = b\,\mathrm{e}^{-kx} \tag{2}$$

Figure 3. Phosphine decay curve in the smoking chamber. Experimental points were interpolated by an exponential equation.
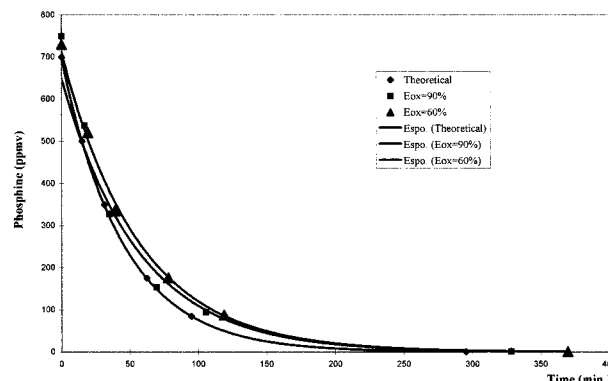

Figure 4. Experimental curve trend obtained for E_{ox} values between 60% and 90% compared to the theoretical curve.

which in our case is transformed into the equation

$$C_t = C_0\,\mathrm{e}^{-kt} \tag{3}$$

where C_t is the concentration of phosphine in the smoking chamber over time, C_0 is the concentration of phosphine in the smoking chamber when t is equal to 0, t represents time, and k is a constant value.

The constant k takes into consideration the flow used in the recycling system, the volume of the chamber, and the oxidative efficiency of the oxidizing solution. Therefore, eq 3 becomes

$$C_t = C_0\,\mathrm{e}^{-E_{ox}(\Phi/V_0)t} \tag{4}$$

where Φ is the flow (V/t) of the pump, V_0 is the volume of the smoking chamber, and E'_{ox} is the efficiency of the oxidation, as defined in eq 1, divided by 100 ($E_{ox}/100$).

In Figure 4, the theoretical and experimental curves obtained with an E_{ox} between 60% and 90% are reported. As can be seen, in all three cases the experimental curve diverges from the theoretical one. To describe the experimental curve using eq 4, it is necessary to introduce an additional factor; thus eq 4 is modified as

$$C_t = C_0\,\mathrm{e}^{-aE_{ox}(\Phi/V_0)t} \tag{5}$$

from which

$$t = \frac{V_0}{aE_{ox}\Phi}\frac{\ln C_0}{C_t} \tag{6}$$

where a takes into account a series of factors such as

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Table 3. Experimental Values of Parameter *a* Obtained in Three Different Experimental Conditions

condition	exptl values of parameter *a*			average
I	0.57	0.61	0.63	0.60
II	0.73	0.70	0.74	0.72
III	0.81	0.79	0.76	0.79

the effect of diffusion, the temperature, and the structure of the recycling system, as reported in Figure 2.

To apply eq 5 to experimental cases, it is necessary to know the value of parameter *a*. For any particular structure of the recycling system it is possible to experimentally determine the relative value of *a*. To do this, when the initial concentration of C_0 is known, it is necessary to measure the concentration of phosphine several times within an appropriate interval, substitute the resulting values of the concentration in eq 5, and solve it with respect to *a*. In Table 3, three series of values are reported for *a*, which were obtained for three different structures of the recycling system. As can be seen, the average values are not comparable; even if the average values diverge, a moderate efficiency in reducing phosphine is guaranteed in any case; the closer the value of *a* is to 1, the shorter the time required for the complete reduction of phosphine. From the results obtained, it can be deduced that, if the structural and operative features do not change for a system, the value of *a* remains constant.

Equation 6 makes it possible to calculate the time necessary for the oxidation of phosphine following the smoking process. Since the time required for the reduction of phosphine is directly proportionate to the volume of the chamber, it makes sense to operate with ratios close to 1:1 between the volume in question and the apparent volume of the foodstuffs to be smoked. When parameters such as *a*, E'_{ox}, and Φ increase, an inversely proportionate decreasing in time of the oxidation treatment results. While *a* and E'_{ox} can become 1 at the maximum, the flow may, theoretically, assume an infinite value. For this reason, it is a good idea to increase the flow as far as is compatible with the system. As time is a logarithmic function of the ratio between C_0 and C_t, it makes sense to work with low initial concentrations of fumigant, compatibly with the efficiency of the smoking process, to minimize the time required for its subsequent reduction.

The study of eq 5 also leads to the following considerations: each time a volume of gas which is equal to the volume of the smoking chamber undergoes an oxidative process, the concentration of phosphine decreases by a constant factor which does not depend on either the initial concentration or the volume of the smoking chamber. This tends to e (the basis of natural logarithms) when the product aE'_{ox} tends to 1, in the ideal case.

CONCLUSIONS

Following the fumigation process, phosphine residues can be oxidized to a nonvolatile and easily disposable phosphorus compound, instead of being dispersed into the atmosphere. Under laboratory conditions, we proved that the oxidation of phosphine can be carried out using inexpensive solutions of potassium permanganate or potassium bichromate containing small quantities of silver ions as a catalyst. The recycle system described makes it possible to reduce the concentration of phosphine to a prefixed value, irrespective of the oxidative efficiency of the oxidizing solutions and avoiding any dispersion of the fumigant into the atmosphere. Finally, as the mathematical function describing the changes in the concentration of phosphine during the reduction process was known, it was possible to identify what parameters needed to be taken into consideration in order to reduce to a minimum the time needed for the disposal of phosphine.

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