MOISTENED CHARCOAL (WITH OR WITHOUT COPPER SULPHATE) – A POTENTIAL SCRUBBER FOR PHOSPHINE

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ABSTRACT

Regulations place constraints on levels of phosphine (PH_3) that may be emitted from fumigation processes. Activated charcoal is a potential absorbent for use as fumigant scrubbers. Absorption of PH_3 by activated charcoal is enhanced by the presence of water and/or copper sulphate. To meet workspace or environmental limits while venting fumigations to atmosphere, moist activated charcoal without the addition of copper could be used to construct a scrubber. Without the addition of copper the scrubber would be marginally less effective, but this would be repaid by a reduction in the costs of construction and simplified disposal of waste from the scrubber.

The absorption of PH_3 on dry charcoal is exothermic and can lead to combustion. However, in prototype scrubbers moist charcoal dosed with high levels of PH_3 did not present evidence of a fire hazard. Pressure tests with charcoal granules have indicated that realistic flow rates can be achieved for scrubbing PH_3 from large grain storages. A small prototype scrubber was tested with a 70 m^3 fumigation chamber and a 50 tonne silo. Practical engineering parameters for the design of large commercial scrubbers require further work.

INTRODUCTION

Phosphine (PH_3) is widely used to control insect pests in stored-products, particularly cereal grains. Its use has enabled Australia to satisfy market requirements for insect free grain. However the recent restriction on the use of methyl bromide under the Montreal Protocol has highlighted the vulnerable position of fumigants for use in controlling stored-product insects.

In Australia, PH_3 is commonly used for fumigation either in sealed storages or applied continuously at low concentrations in unsealed storages (e.g. SIROFLO®, Winks and Russell 1994). With either practice, there is loss of PH_3 to the atmosphere. In sealed storages, PH_3 is released to atmosphere when the grain bulk is aired and is lost through relief valves that accommodate diurnal changes of temperature and pressure. With SIROFLO® there is a continuous low-level emission during the course of the fumigation.

Permissible workplace levels, in most countries, are set at 0.3ppm v/v (0.42 mg m^{-3}) time weighted average (TWA) (e.g. ACGIH 1993; NOHSC 1991), but in some countries are lower (e.g. 0.1 ppm in Germany). Regulations for maximum

permissible levels in the environment around fumigations are lower; typically at least 10 times less than the workspace value, for instance in the State of Victoria, Australia, ground level concentrations should not exceed 0.0042 ppm (Victorian Government Gazette 1981) and environmental levels of 3 ppb have been suggested throughout Australia (NHMRC 1992). While current fumigation practices are able to meet these requirements, increasing PH_3 dose to combat rising insect resistance and coincident lowering of workspace or environmental limits may necessitate the need to reduce emissions to atmosphere. In 1994, Banks made a timely warning 'not to be complacent about the future use of phosphine' as its future use was threatened by environmental and workspace restrictions, pest resistance, its known toxicity to humans and accidents.

While little has been published on use of absorbents to remove of PH_3 from air, it is known that PH_3 reacts rapidly with solutions of sodium hypochlorite (Lawless and Searle, 1962) and potassium permanganate. A potassium permanganate scrubber has been used by BOC Gases in Australia to dispose of residual PH_3 from gas cylinders (Ryan, pers. comm. 1998). Some zeolite products are effective for the absorption of PH_3 (Kuznetsova *et al.*, 1996). However, the cost of these materials may preclude their use on a large scale.

Ideally, a material for trapping fumigant should be highly absorbent, inexpensive, readily regenerated and should not create a subsequent disposal problem. Use of charcoal or activated carbon would appear to be the most likely and practical candidate for the absorption of fumigant PH_3. Activated carbon or charcoal, usually with added copper salts, has been reported in the literature as capable of removing PH_3 from gas mixtures. Andreev and Kavtaradze (1949) observed the catalytic oxidation of PH_3 on dry charcoal in the presence of copper salts. Similar mixtures were evaluated as absorbents for PH_3 (Muthu, *et al.* 1974; Rakitskaya *et al.* 1987; Shengeliya *et al.*, 1982; Guo *et al.*, 1993) and have been patented for use as gas mask filters to exclude PH_3 (Heidrich and Lemke, 1960). Recent studies found that PH_3 absorption by carbon was increased by the presence of oxygen and water (Kuznetsova *et al.* 1996); it is assumed that this is due to the oxidation of PH_3. Oxidation of PH_3 is an exothermic reaction and it is generally assumed that the product is phosphoric acid.

The published work has been largely concerned with removal of PH_3 as a low level impurity in other gases and is difficult to compare because of the many differences in substrates, additives and sorption conditions. The present study looks at removal of PH_3 (at fumigant concentrations) from gas flows in anticipation of future requirements for reducing PH_3 emissions to acceptable levels.

MATERIALS AND METHODS

Sorption materials

The absorbents studied were; charcoal, charcoal with copper additives, natural zeolite and natural zeolite with copper additives. Marble chips, assumed to be relatively inert with respect to absorbent behaviour, were used as a control.

Charcoal: Two grades of charcoal were used in these experiments, 14-25 mesh and 8-16 mesh. Both were designated Type 16, and were suitable for use in respirator canisters. Results of analysis of this charcoal undertaken by Consulchem Pty. Ltd. (Australia) are given in Table 1.

Charcoal with copper additives: Charcoal with 5% copper powder (w/w) was prepared by admixture of copper powder to the charcoal. Copper powder was freshly prepared by treatment of a stirred aqueous solution of copper sulphate with fine zinc powder. The precipitated copper powder was collected by vacuum filtration, rinsed and dried in a vacuum desiccator.

TABLE 1
Laboratory report on charcoal

Test	Specification	Result
CTC	Carbon tetrachloride	34.9%
Iodine No.	ASTM D4607-86	881
Ball Pan Hardness	ASTM D3802-79	98.4
Phenol	AWWA 3600-78, Appendix B	13.5g L-1

Charcoal with copper sulphate was prepared by mixing a saturated solution of copper sulphate with charcoal, then collected by vacuum filtration and air-dried to obtain charcoal impregnated with copper sulphate.

The charcoal and charcoal/copper absorbents were dried at 150°C under stream of nitrogen (100 mL min^{-1} for 2-3!h) before use.

'Moist' charcoal: 'Moist' charcoal was prepared by stirring charcoal in distilled water then filtered off and air-dried. This resulted in charcoal with moisture content of approximately 35% w/w. Moist charcoal was used without further drying.

Zeolite: Zeolite (clinoptilolite) was obtained from Currumbin Sand and Gravel, Qld, Australia, and sieved to obtain 14 to 25 mesh particle size. This zeolite was unrefined and was chosen because it was cheap and readily available in Australia. Zeolite impregnated with copper sulphate was prepared in the same manner as that described above for charcoal.

Phosphine
Phosphine, 1,500 ppm in nitrogen (BOC Australia), was diluted with instrument grade air to the desired concentration and flow rate using mass flow controllers (Brooks 5850E series).

Measurement of absorbent capacity
Initial studies were carried out with dry activated charcoal (8-16 mesh) in a stainless steel tube (110 mm × 7.5 mm i.d.) without additives. Further comparative tests were carried out using slightly larger stainless steel tubes (300 mm x 16 mm i.d.). Charcoal or zeolite absorbents were held in place within the (300 mm x 16 mm i.d.) tubes by a 48 mesh stainless steel disc at each end. To reduce the risk of gas channelling along the interior wall of the tube, each tube also contained a stainless steel spring (200 mm x 16 mm). The weight of each absorbent used in comparative studies varied but the length of the column and the mesh size (16-25) were constant. With the exception of moist charcoal, the absorbents were conditioned *in situ* by heating to 160°C overnight (15 h) in a stream (100 mL min^{-1}) of dry air. Phosphine (720 ppm) was passed through the

absorbents at 100 mL min^{-1} or 500 mL min^{-1} and the PH$_3$ levels in the effluent gas were monitored to obtain a breakthrough time and emergence profile. Phosphine concentrations were measured with a Bedfont EC80 Electrochemical Detector. When humid air was required the dry air was passed through two gas washing bottles in series containing distilled water.

Comparison of absorbents
Tubes packed with absorbents were mounted vertically and connected in parallel as shown in Fig. 2. Valves (S1, S2, S3 and S4) were controlled by computer so that the gas emitted by each tube was either vented to air or directed to the detector ('Det.' in Fig. 2). Gas flows through the absorbent filled tubes were nominally the same (usually 100±2 mL min^{-1}) and were balanced using tubing clamps on the inlet tubes. The exhaust gas from each tube was monitored over a twelve-minute period every hour, and PH$_3$ concentrations recorded every two minutes via an Amasco phosphine detector (with a Citicel electrochemical carbon monoxide sensor). Confirmation of input and output PH$_3$ concentrations was obtained by taking samples from sampling ports located at the inlet and outlet of each tube. These samples were measured against gas standards using a gas chromatograph fitted with a flame photometric detector.
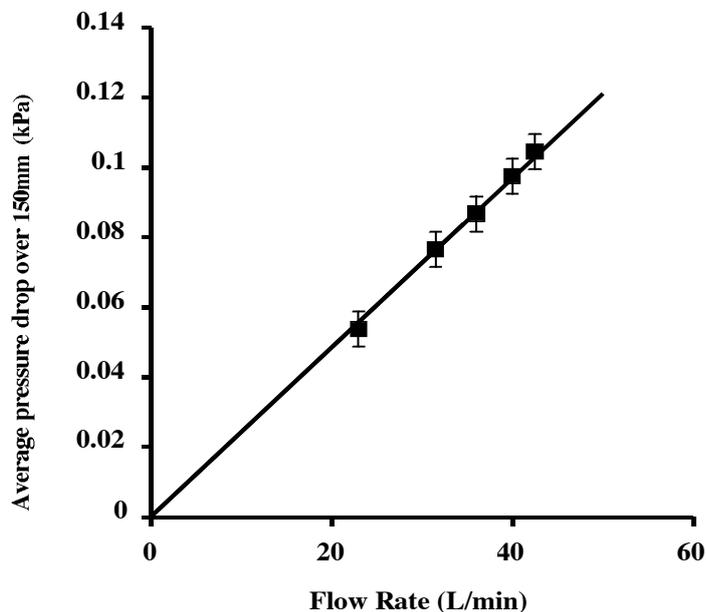

Fig. 1. Pressure drop across a 150 mm bed of charcoal (Type 16, Grade 14-25) at various flow rates. Each point is the average of four measurements (s.d. shown as error bars) taken at 150 mm intervals on a 1.0 m × 150 mm column of charcoal.
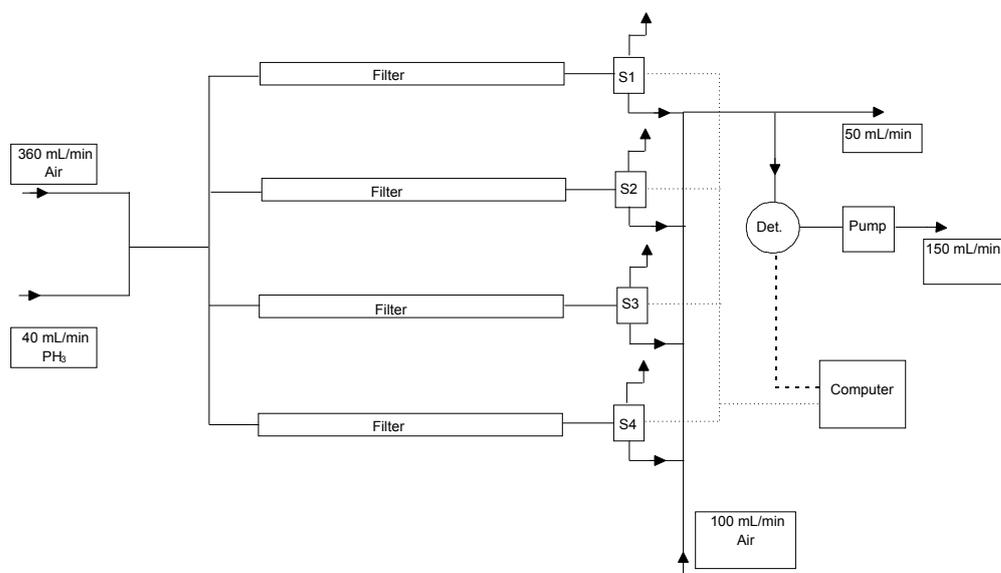
Fig. 2. Flow diagram for comparison of absorbents. The phosphine was delivered from a cylinder of phosphine (10 mg mL^{-1}) in nitrogen and mixed with air to provide a phosphine concentration of about 800 ppm.

Measurement of pressure loss in air flow through a charcoal bed
Pressure loss in an airstream through charcoal (14–25 mesh) was measured in an apparatus similar to that described in International Standard ISO 4174 (ISO 1980). The charcoal was supported on 1.5 mm mesh above a 1 m plenum in an upright 2 m tube (150 mm i.d.) so that the charcoal filled the upper 1 m of the tube. Test points were placed in the side of the tube at intervals 150 mm. Air was blown into the bottom of the tube at a known flow rate and the pressure, relative to ambient, was measured at each test point. The flow into the tube was measured with a GA Platon Gapmeter and the pressure at each test point was recorded with a U-tube manometer and a Halstrup EMA84 Digital manometer (0-1.0 kPa). Pressure drops across each 150 mm of charcoal bed were averaged and plotted against flow rate (Fig. 1).

Analysis of carbon samples
Solid carbon samples were analysed for copper, phosphorus and sulphur by X-ray fluorescence spectrometry of pressed discs. In addition, freshly dried samples (4.5 g dry weight) were extracted with water in a Soxhlet apparatus for 24 h. The aqueous extracts were concentrated and made up to 50 mL with 4% nitric acid. These solutions were analysed for copper by atomic absorption spectrometry and for phosphorus colorimetrically using a Technicon (II) Autoanalyser.

Scrubbers
A prototype scrubber, as shown in Fig. 3, was constructed for field testing. The scrubber consisted of a 44 gallon (205 L) drum fitted with a central diffuser (80

mm i.d.) which allowed the input air stream to flow radially and longitudinally through 14-25 mesh activated carbon.

The scrubber was tested against an airstream containing 200 ppm PH$_3$ presented at the rate of 4 g h^{-1} and 400 ppm at the rate of 8 g h^{-1} for 14 days. Phosphine levels in the input and output airstreams were monitored with an electrochemical hydrides monitor calibrated for phosphine.
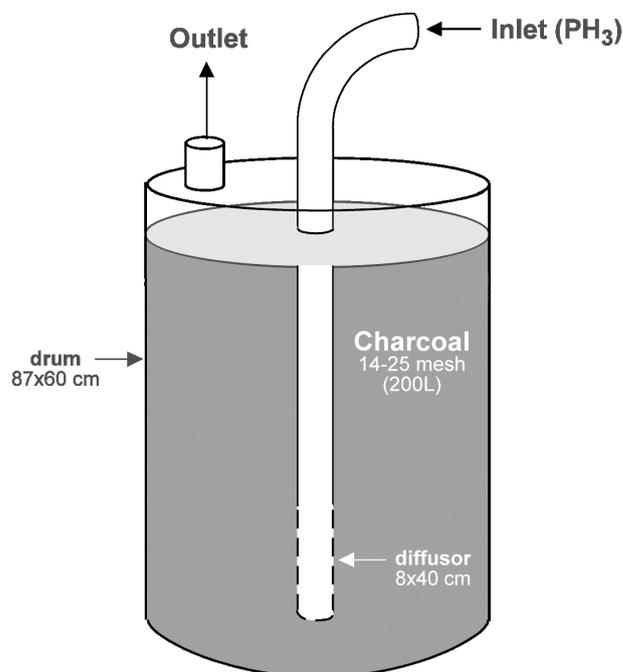

Fig. 3. Prototype scrubber for phosphine.

Prototype scrubbers were constructed from fibreglass drums (steel drums are corroded by contact with both copper sulphate solution and phosphoric acid, which may be a by-product of the scrubbing process) (0.6 m diam. _ 1.0 m, 280 L) containing 22.5 kg of 14-25 mesh charcoal (34 L) supported on a fine mesh to give a plenum below the charcoal bed. The charcoal was pre-treated with copper sulphate solution. The breakthrough characteristics of a single scrubber were tested using an empty 50 tonne sealed silo where the atmosphere in the silo could be recirculated (by means of a fan (Dawn 3.5B) running at 6 m^3 h^{-1}) either through, or bypassing, the scrubber. Two of these scrubbers (in parallel) were used in a trial to remove phosphine from a chamber (12.5m x 2.5 m x 2.5 m) used to fumigate cut flowers.

RESULTS AND DISCUSSION

Initial studies were carried out with dry activated charcoal (8-16 mesh) without any added materials. Results shown in Table 2 are from a tube (110 mm × 7.5

mm i.d.) of active carbon presented with 100 ppm PH_3 at various flow rates. The PH_3 was trapped at 100 mL!min^{-1} but when the flow was increased breakthrough occurred. Breakthrough was prevented at these concentrations and flow rates, by reducing the particle size of charcoal to 14–25 mesh. A similar result might have resulted if the contact time between the gas flow and charcoal was increased either by increasing the size of the charcoal bed or reducing gas flow.

TABLE 2

Phosphine concentrations emitted when 100 ppm phosphine was passed through a tube (110 mm × 7.5 mm I.D.) of 8-16 mesh active carbon for three minutes at a range of flow rates

Flow (mL min^{-1})	PH_3 in effluent (ppm)	% PH_3 removed by passage through charcoal
100	0	100
200	14	93
300	40	87
400	75	81
500	85	83

Using the finer 14-25 mesh charcoal, 720 ppm PH_3 at 100!mL!min^{-1} was successfully trapped without breakthrough for 15 h on 33g of activated charcoal. Higher backpressures due to increased resistance to gas flow are a disadvantage of deep absorbent beds and small mesh sizes. Backpressure is an important consideration in the design of a scrubber. For example, calculations on possible peak flows from four, 0.2!m diameter, relief valves on a sealed 54,000 tonne shed indicated face velocities of 1.6!m!sec^{-1}. If this flow is to be scrubbed by radial passage through a column of absorbent 2!m by 0.5!m diam. then outlet flows with a face velocity of 0.5!m!min^{-1} could be expected. In order to avoid damaging the sealing of the shed, backpressure created by the scrubber must not exceed 200!Pa, and preferably should be less than this. Backpressures created by airflow through the 14-25 mesh carbon are shown in Fig. 1 for gas flows in the range 0-45!L!min^{-1} having face velocities in the range 0-2.5!m!min^{-1}. As these backpressures were acceptable at the flow rates likely to be encountered under field conditions, all further work was carried out using material of this mesh size.

The behaviour of activated charcoal in response to changed input PH_3 concentration and flow rate is given in Table 3. A PH_3 concentration of approximately 800!ppm at 100!mL!min^{-1} was passed through a tube of active carbon and the output concentration was monitored. Breakthrough was recorded after 15!h, following, which the output concentration climbed and steadied at about 480!ppm after 30!h. When the input concentration was reduced by half, to 400 ppm, the output concentration dropped by almost half to about 230!ppm. The results are consistent with a slow rate of absorption (or reaction) of phosphine where the amount of PH_3 absorbed depends on contact time with the absorbent. Thus at 100!mL!min^{-1} approximately 40% of the PH_3 is absorbed for both 800 and 400!ppm input concentrations. However when the flow rate was reduced to 50!mL!min^{-1}, nearly 60% of the PH_3 was absorbed.

TABLE 3

Phosphine emission from a 300 × 16 mm I.D. tube of 14-25 mesh active charcoal for
different input concentrations and flow rates

Flow rate (mL!min^{-1})	Input Conc. (ppm)	Output Conc. (ppm)	PH$_3$ sorbed (%)
100	804	484	40
100	402	234	42
50	720	312	57

When the tube was subsequently flushed with phosphine-free air there was no evidence of PH$_3$ being emitted from the carbon. When the tube was baked at 135 C only a very small amount of PH$_3$ was emitted over about 2!h. This indicates that PH$_3$ is irreversibly absorbed or reacted on the absorbent.

In an effort to improve the sorptive ability of the charcoal and prevent or minimise breakthrough, the effect of copper additives were investigated. The behaviour of charcoal compared with charcoal containing 5% copper powder is shown in Fig.!4. The addition of copper increased the removal of PH$_3$ from the air stream. Copper sulphate was similarly successful in promoting the sorptive ability of the activated carbon, however the improved performance cannot be attributed to the copper alone. Zeolite (clinoptilolite) with added copper salts did not remove phosphine from gas flows (Fig.!5).
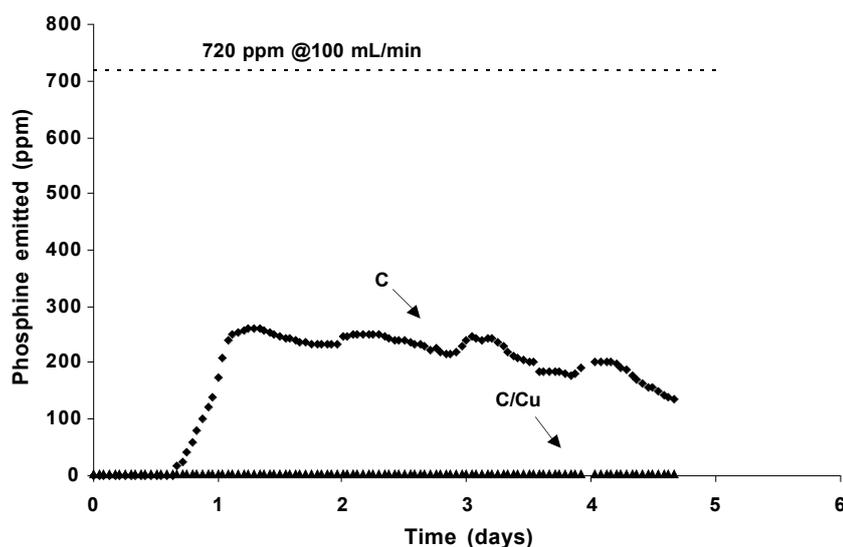

Fig. 4. Comparison of the emission of phosphine from tubes of Carbon (♦)and Carbon with 5% Copper powder (▲) when supplied with 720 ppm phosphine at 100 mL min^{-1} (----)
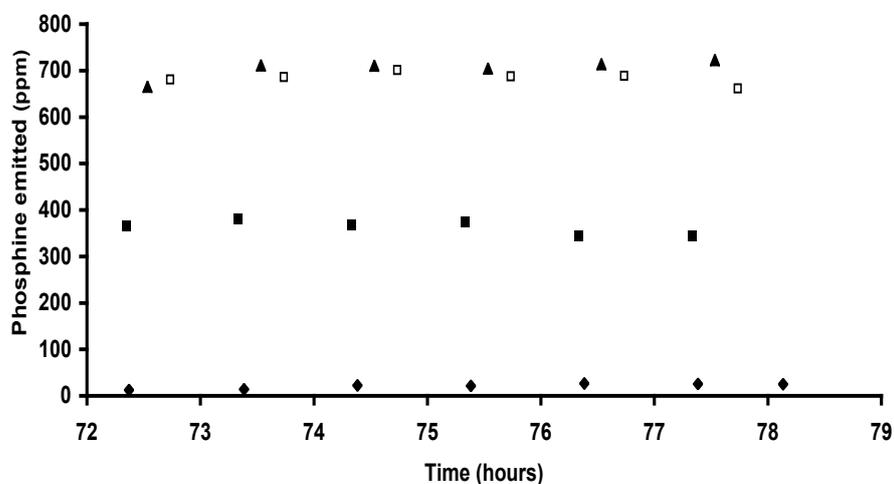
Fig. 5. Emission of phosphine from tubes of Carbon (—), Carbon+CuSO$_4$ (♦), Zeolite+CuSO$_4$ (▲) and Marble chips (□) after three days treatment with 720!ppm phosphine at 100 mL min^{-1}.

The experiments discussed so far were carried out using 'instrument grade' cylinder air and nitrogen with a very low relative humidity. In practice, the scrubber would be used under ambient conditions so it was important to determine the effect of water vapour on the absorptive capacity of activated carbon. Fig. 6 shows the results of a comparison of carbon and carbon/copper sulphate as absorbents for PH$_3$ using both 'dry' (as previously used) and moist (humidified) inlet gas. Surprisingly, the presence of water was found to enhance the capacity of the active charcoal to remove PH$_3$. The improved efficacy with added water may explain the apparent improvement in the efficacy of active carbon with time seen in Figs.!4 and 6 when PH$_3$ was added in 'dry' air. Absorption of small amounts of water vapour from the 'dry' air over time would slowly enhance the ability of the carbon to remove PH$_3$. This is consistent with the findings of Kuznetsova et al. (1996) that PH$_3$ is irreversibly absorbed on carbon in the presence of oxygen and water vapour. If a reduction in outlet PH$_3$ concentration is required to meet workspace or environmental regulations, moist activated charcoal may be sufficiently efficient without the addition of copper. In turn, the removal of copper from the scrubber would reduce the cost of construction and disposal of waste from the scrubber.
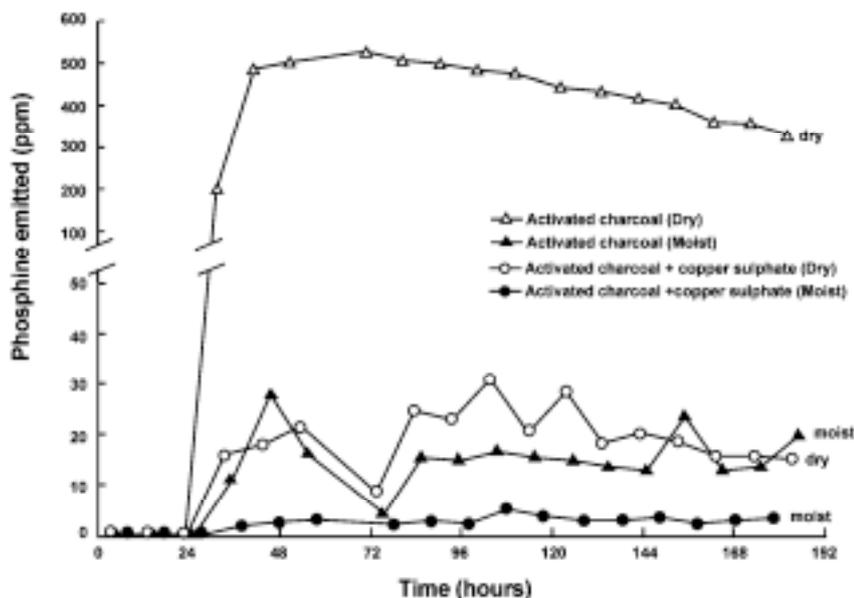
Fig. 6. A comparison of the abilities of carbon and carbon+copper sulphate to absorb phosphine from humid (Moist) and dry air.

The fate of PH_3 on activated carbon is not known although Kuznetsova *et al.* (1996) suggest that PH_3 is oxidised to phosphate. The fact that very little PH_3 is recovered on heating the carbon after exposure would indicate that the PH_3 has reacted or is permanently chemisorbed. If exposed carbon is washed with water the aqueous extract is acidic. The levels of phosphorus, copper and sulphur for some extracts and samples of carbon/copper sulphate, before and after exposure to PH_3, are given in Table 4. These data show that the phosphorus absorbed is removed by extraction with water, which is consistent with the PH_3 being oxidized to phosphate. Moreover these results indicate that it should be possible to refresh the absorbent by washing, drying and retreating with copper sulphate solution.

TABLE 4

% (w/w) soluble and insoluble phosphorus, copper and sulphur in samples of carbon/copper sulphate, before and after exposure to phosphine (1.0 mg L^{-1})

Sample	Phosphorus	Copper	Sulphur
Unexposed C/CuSO$_4$	0.043%	2.7%	1.4%
C/CuSO$_4$ after exposure to 1.0 mg L^{-1} PH$_3$ at 100 mL min^{-1} for 5 days	2.27%	n.a. [†]	n.a. [†]
Water soluble material extracted from exposed C/CuSO$_4$	2.1%	1.9%	n.a. [†]
Exposed C/CuSO$_4$ after extraction	0.13%	0.4%	0.03%
Unexposed C/CuSO$_4$ after extraction	0.018%	n.a. [†]	n.a. [†]

[†] n.a. not analysed

The capacity of carbon/copper sulphate or moist charcoal to absorb PH_3 has not been exceeded in the experiments carried out in this study. When 4.59 g of carbon/copper sulphate was treated with successive 5 mL injections of 85% PH_3 in a sealed flask (100 mL), with air permitted to enter the flask after each addition, the PH_3 continued to be absorbed. After 37 additions over 7 days, approx. 0.26 g of PH_3 (or 5.7% w/w) was absorbed. If the absorbent is acting to catalyse the oxidation of PH_3 to phosphorus oxy-acids, the absorbent may effectively be inexhaustible.

Colabella *et al.* (1988) studied the 'adsorption and subsequent oxidation' of PH_3 on activated carbon, a reaction which is known to be exothermic. The maximum temperature reached during adsorption of PH_3 (10% PH_3 v/v in H_2) in the absence of oxygen was 53°C. However, the maximum temperature reached during subsequent oxidation was 198°C (dependent on the flow rate of oxygen). It has also been noted (Ren, pers. comm. 1998) that during the rapid addition of high concentrations of PH_3 in air (10 mg L^{-1} or greater) to small amounts of carbon, that the heat of reaction can be sufficient to cause the carbon to glow red-hot. Nevertheless, in the many experiments carried out during the present study, using concentrations 1 mg L^{-1} (720 ppm) or less, there were no instances of excessive heat generation, ignition or explosion.

A prototype PH_3 scrubber (Fig. 3) was tested with a PH_3 generator capable of delivering known amounts of PH_3. The scrubber proved to be effective in removing PH_3 at concentrations of 200 ppm presented at the rate of 4 g h^{-1} for 14 days. At no time did the PH_3 concentration in the effluent air exceed 0.3 ppm. The scrubber was also effective in keeping effluent gas below 0.3 ppm when tested with PH_3 at 400 ppm, 8 g h^{-1} for 7 days.

A second scrubber was built to reduce the amount of PH_3 released from a fumigation chamber after commercial fumigation of cut flowers prior to export. It was calculated that the 70 m^3 fumigation chamber would require a scrubbing bed containing 444 kg of moist charcoal (2.3 m^2×0.31 m) to absorb, without breakthrough, 720 ppm PH_3 from air circulated at one complete air exchange per hour (70 m^3 h^{-1}) with a back pressure of less than 40 Pa. It was not immediately possible or practicable to construct a scrubber of these dimensions and a scrubber using one tenth of the calculated amount of charcoal/$CuSO_4$ was constructed from materials at hand. This scrubber was tested using an empty 50 tonne sealed silo (approx 70 m^3) where the atmosphere in the silo could be recirculated through the scrubber. A PH_3 concentration of 740 ppm was established in the silo and the gas concentration was monitored between the silo and the fan. With the scrubber 'off line' the measurements indicated PH_3 concentrations in the silo; with the scrubber 'in line' the measurements indicated breakthrough concentrations emitted by the scrubber. Figure 7 shows the PH_3 concentration measured before the scrubber was placed 'in line' and subsequently the output or breakthrough concentration from the scrubber.

In the field two identical scrubbers were used in parallel on the 70 m^3 fumigation chamber. The fumigation chamber was fitted with fans capable of providing up to three air exchanges per hour. Phosphine at 735 ppm was applied to cut flowers, dropping to 500 ppm at the end of the fumigation. The atmosphere was then circulated through the twin scrubbers for 1.5 h to reduce the PH_3 concentration. Notwithstanding the smaller than optimum size, the scrubbers were effective in reducing the PH_3 levels in the chamber to levels below 150 ppm within two hours.
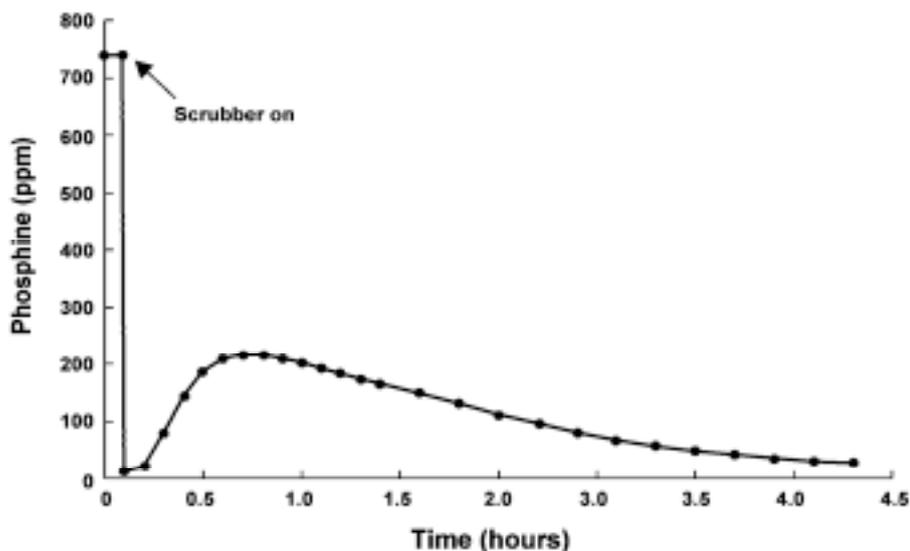
Fig. 7. Breakthrough behaviour of a scrubber during the removal of phosphine from a 50 tonne silo. The scrubber contained 22.5!kg of 14-25 mesh charcoal/CuSO$_4$ in a plastic drum with fumigant atmosphere circulating at 6!m^3! h^{-1}.

CONCLUSIONS

The aim of this study was to find an absorbent for PH$_3$ that could be used for scrubbing PH$_3$, vented from fumigations, to meet workspace and environmental limits. Although passing the outlet gas through moist activated charcoal is marginally less effective in removing PH$_3$ than moist activated charcoal with the addition of copper, this would be repaid by a reduction in the costs of construction and simplified disposal of waste from the scrubber. If greater efficiency in the removal of PH$_3$ from gas flows were required then the addition of copper or copper sulphate to the moist activated charcoal would be indicated.

Effective scrubbing requires sufficient contact time with the active charcoal to catalyse an oxidation reaction that can be further promoted by copper and water. Use of carbon absorbents in a commercial PH$_3$ scrubber will require engineering and research and development to determine the structural design parameters. Parameters such as; the!depth of the absorbent bed, the flow rate through the bed and the mesh size of the charcoal particles will need to be considered in developing a scrubber for phosphine at industrial flow rates (without excessive back pressures). It will also be necessary to determine rates of sorption that will not generate excessive amounts of heat from exothermic oxidation of the PH$_3$.

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