# Phosphine generator trial using external air dilution

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Abstract

A commercial phosphine ($PH_3$) generator manufactured by Beijing Liangmao Technology Development Company Limited, China was used in a fumigation trial on 5000 tonne bunker storage. The generator's production of $PH_3$ is controlled by the rate of dosing conventional aluminum phosphide (AlP) tablets into 100 kg water in the reaction chamber.

Because $PH_3$ is flammable and explosive if certain a concentration is reached in air, it is usually mixed with carbon dioxide ($CO_2$) in the weight ratio of 50:1. This trial's objective was to minimise the amount of $CO_2$ and dilute the generated $PH_3$ with air. The $PH_3$ generated is purged from the reaction chamber by a continuous low flow of regulated $CO_2$ gas. The $PH_3$-rich $CO_2$ purge stream was fed into the suction inlet of an external venturi. A high pressure fan was used to produce the air flow through the venturi to create the vacuum to suck in and dilute the $PH_3$ rich stream from the generator. The $PH_3$ was diluted in the air-flow to ensure a non-flammable concentration of less than 1% (10.000 ppm) and thence fed directly into the bunker storage. The trial successfully demonstrated the viability of generating phosphine in this manner, and excellent results in $PH_3$ concentration and distribution was achieved in very short time periods. The capacity of the generator was limited to 8 kg of AlP tablets, equivalent to 2.667 kg of $PH_3$, or sufficient to fumigate 2667 $m^3$ of grain at a dosage rate of 1 $g/m^3$. A much larger version of the machine would be required to fumigate medium size bunker storages in the 10.000 to 15.000 tonne range. Notwithstanding, the generator offers an attractive package combining the speed and convenience associated with the use of gaseous $PH_3$ with the low cost of AlP formulations.

Keywords: Phosphine fumigant, On-site generator, Metallic phosphide, Non-flammable

## *1. Introduction*

The preferred fumigant for stored product insect in bulk grain is phosphine because it is the lowest cost fumigant when generated from solid metallic phosphide products (usually aluminium phosphide: AlP). The major hazard concern with phosphine is its wide range of flammability with a lower flammability limit of 1.8% in air. Another issue with $PH_3$ is its approximate 5 day exposure time which is extended by the 1-2 days required to generate $PH_3$ gas from AlP tablets reaction with atmospheric moisture.

$PH_3$ was mostly generated in-situ from AlP tablets until the commercial availability of $PH_3$ as a compressed gas [either as 100% or non-flammable mixtures of $PH_3$ in $CO_2$ (2.6 vol%) or nitrogen: $N_2$ (2.0%)].

On-site $PH_3$ generators allow the quick release of $PH_3$ from AlP tablets by dropping the tablets into water; however this exacerbates the flammability issue. One solution is to purge with large volumes of $CO_2$, however the additional number of cylinders required adds cost and complications in remote locations ($N_2$ cylinders can be substituted for $CO_2$ however this required three times the number of gas cylinders). While some $CO_2$ cylinders are required for pre-purging and post-purging the reactor, the required number is significantly reduced by mixing the generated $PH_3$ with air prior to release into the storage to be fumigated. While related techniques can be used, this trial used a venturi which allowed the intimate mixing of $PH_3$ and air to a non-flammable level of less than 10.000 ppm prior to discharge into the grain storage.

*2. Materials and methods*

A commercial $PH_3$ generator manufactured by Beijing Liangmao Technology Development Company, China was used in the fumigation of 5000 tonnes of wheat. The generator's production of $PH_3$ is controlled by the rate of dosing conventional Aluminum phosphide (AlP) tablets into 100 kg water in the reaction chamber. The maximum rate of dosing is 24 tablets/minute (24 g of $PH_3$/minute = 72 g of AlP/minute). The recommended capacity of the generator was 8 kg of AlP tablets, equivalent to 2.667 kg of $PH_3$, or sufficient to fumigate 2667 $m^3$ of grain at a dosage rate of 1 $g/m^3$.

Because $PH_3$ is flammable and explosive over 1.8% [18000ppm] $PH_3$ it is usually mixed with $CO_2$ in the weight ratio of 50:1 (2% by weight $PH_3$ in $CO_2$ is non-flammable). This trial's objective was to minimise the amount of $CO_2$ and dilute the generated $PH_3$ with air. The $PH_3$ generated is purged from the reaction chamber by a continuous low flow of regulated $CO_2$ gas. The $PH_3$-rich $CO_2$ purge stream is fed into the suction inlet of an external venturi. A high pressure fan was used to produce the air flow through the venturi to create the vacuum (1 kPa) to suck in and dilute the $PH_3$ rich stream from the generator. The $PH_3$ was diluted in air flow to a non-flammable concentration of less than 1% (10,000 ppm) prior to delivering this air to the bunker storage.

The measurement of the $PH_3$ was achieved with commercial instruments used by field fumigators [MiniWarn – Draeger; Silo Chek – Canary Co]. Dilution equipment was prepared which was capable of ten times dilution in air of any $PH_3$ samples greater than 1000 ppm to keep within the range of the electrochemical instruments used.

*3. Results*

The trial successfully demonstrated the viability of generating phosphine in this manner, with excellent results in $PH_3$ concentration and distribution of non-flammable $PH_3$ gas was achieved in very short time periods (~4 hours, Figures 1 and 2). The generator was operated at its maximum dispensing rate of 24 tablets/minute (24 g of $PH_3$/minute = 72 g of AlP/minute). In excess of 50 samples were taken to monitor the $PH_3$ level in the air flow into the bunker grain storage. The cumulative $PH_3$ produced is graphically presented in Figure 1, and shows 80% is obtained within 3 h and 100% after 6 h. The $PH_3$ concentration (ppm) profile over a seven 7 h period is shown in Figure 2. The peak $PH_3$ concentration measured was 4400 ppm and the irregular peak (at 2 h) was the result of temporary blockage in the tablet dispenser. The "blip" at the end of the 7 h period was the result of a mineral acid addition to determine residual $PH_3$.

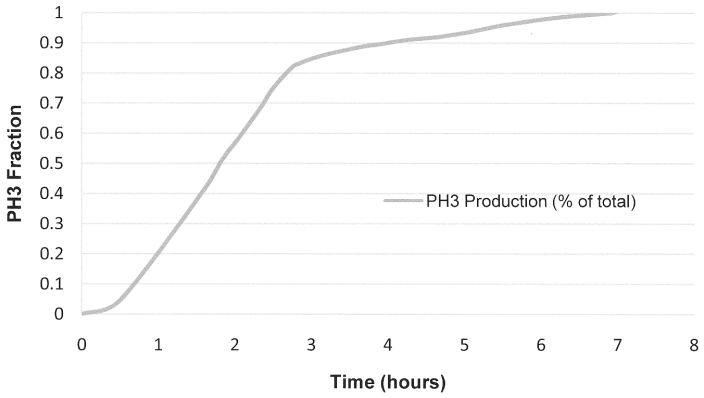


**Figure 1** $PH_3$ generator Trial ($PH_3$ Production - % of total).

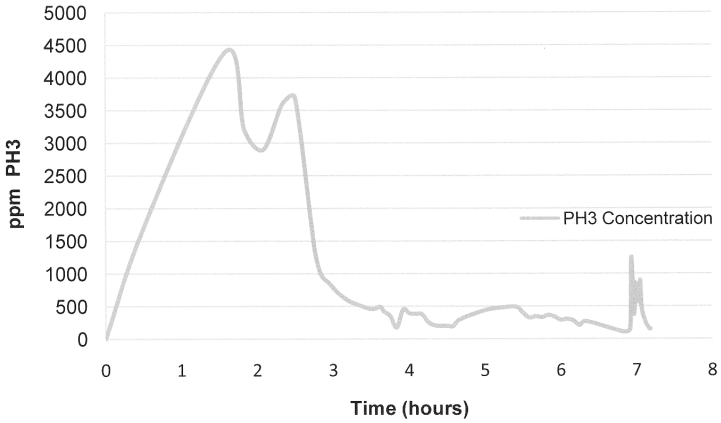


**Figure 2** $PH_3$ generator trial ($PH_3$ Concentration).

The $CO_2$ purge was ~3 kg/h and $PH_3$ generation was ~0.6 kg/h i.e. a ratio of $CO_2$ to $PH_3$ of 5:1 which is a tenfold reduction in $CO_2$ consumption.

*4. Discussion*

The time required to generate $PH_3$, while an order of magnitude improvement on generation from AlP exposure to atmosphere moisture, needs to be further reduced. The capacity of the $PH_3$ generator was 8 kg of AlP tablets, is limited and required "time-out" to prepare additional batches where required.

The field trial demonstrated the need for a larger $PH_3$ generator (5x times the capacity of the unit tested) and reduction of the $PH_3$ generating time.

The purge ratio of $CO_2$ to $PH_3$ of 5:1, a ten-fold reduction in $CO_2$ consumption required for a non-flammable mixture, will need to be maintained but preferably reduced using the proposed larger generator (15 kg $PH_3$).

The much larger version of the $PH_3$ generator is required to fumigate medium size bunker storages in the 10.000 to 15.000 tonne range. Preference is for the re-design unit to incorporate "real time" removal of spent tablet residues with addition of a filter to minimise the scale up required for the reaction chamber.

Notwithstanding, the existing generator offers an attractive package combining the speed and convenience associated with the use of gaseous $PH_3$ with the low cost of AlP formulations.

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