



MEMORANDUM

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HSM-12004

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SUBJECT: RESULTS FROM DOME SAMPLING FOR PHOSGENE USING HIGH INITIAL CONCENTRATIONS OF CHLOROPICRIN (EXTREME CONDITIONS) IN A FIELD ENVIRONMENT

As per your request, we have begun research into the question of in-field conversion of chloropicrin (PIC) to phosgene (carbonyl chloride). The initial approach for using field applications as the chloropicrin source was tabled in favor of a more controlled experimental construction. This controlled set-up would use the static air-limiting accumulation domes (SALAD) placed on untilled soil, with a known amount of PIC added to each dome. This would ensure that PIC was definitely within the SALAD and available for photolytic conversion.

The first attempt, on September 21, used two 25 ml and one 40 ml dosing of PIC across three separate SALADs. The PIC was applied directly to the surface of the soil and the SALAD was placed directly atop the application spot. The PIC was supplied by a local pesticide distributor and was 100% chloropicrin. Two different brands of colorimetric tubes were used to monitor the air concentrations: Sensidyne 172S Chloropicrin colorimetric sampling tubes (range 0.5 to 10 ppm) and Dräger 8101521 Phosgene 0.02/a colorimetric sampling tubes (range 0.02 to 1 ppm). Environmental conditions were favorable for conversion; sunny day with little to no cloud cover.

Results from this experiment were peculiar. Both the PIC and the phosgene tubes showed no measureable materials within the SALAD. This was most confusing, since we knew that a sizable amount of PIC had been added two hours earlier. Several measuring attempts were made using the colorimetric tubes, but all yielded non-detectable results, or so it seemed from the lack of stain along the indicator layer of the tubes.

On returning to the office I contacted Sensidyne technical support. After explaining the conditions of the experiment, they suggested that a “rebleaching” effect was responsible for the anomalous results. This is caused by high concentrations (far beyond the range of the colorimetric tube) of a chlorine-containing test agent overwhelming the pretreatment reagents and entering the indicator tube immediately behind whatever reactants had been formed in the pretreatment section. The unreacted chlorine material bleaches out the dyestuff formed in the indicator tube, and at such high concentrations as were used in this experiment, the forming of



the indicator dyestuff and its subsequent bleaching away were effectively simultaneous. This gave the appearance that no chloropicrin was detected.

A second experiment was conducted on October 25th, with modifications as warranted by the information supplied by Sensidyne. Approximately two milliliters of PIC were added to each of two SALADs (SALAD 1 and 2). Instead of being directly applied to the soil, the PIC was applied to a small plastic surface (underside of plastic drinking cup). One SALAD (SALAD 3) was left empty, to act as a control. The PIC and SALADs were set out at 0925 hours, in full sunlight. An initial sample taken at 1040 hours from SALAD 2 showed high concentrations (15 ppm) of PIC. As a precaution against a repeat of the rebleaching effect, SALAD 1 was lifted momentarily, to reduce PIC levels. Two hours after placement, formal sampling began. The following table summarizes the sampling results:

Table One: Sampling Results for Chloropicrin [PIC] and Phosgene [Phos]

Date	Time	PIC1	PIC2	PIC Control	Phos1	Phos2
10/25/2011	1040	NS	15 ppm	NS	NS	NS
	1115	NS	NS	NS	NS	ND
	1125	6 ppm	4 ppm	ND	ND	ND
	1230	3 ppm	2 ppm	ND	ND	ND
	1330	2 ppm	1 ppm	ND	ND	ND
	1345	Recharged and improved ground seal				
10/26/2011	1030	>16 ppm	>16 ppm	ND	ND	ND
	1200	>16 ppm	>16 ppm	NS	ND	ND
10/27/2011	1045	6 ppm	4 ppm	ND	ND	ND
	1325	8 ppm	ND	NS	ND	ND

PIC1/Phos1: SALAD 1 PIC2/Phos2: SALAD 2 PIC Control: SALAD 3
 ND: Non detectable NS: No sampling

Since the results on October 25th indicated rapid reduction in PIC concentrations, at the end of the day the SALADs were recharged with approximately 1.5 ml. of PIC. Furthermore, the ground seal between the soil and the contacting rim of the dome was improved by placing loose soil around the dome perimeter and compacting the soil against the dome. The SALADs were left in place overnight. The following day, two more samples were drawn. These showed that the concentration of PIC was higher than 16 ppm (upper limit of indicator tube) but not so high as to trigger the rebleaching effect. Since there was PIC in the SALADs, we decided to let the samplers run one more day. On the final day, October 27th, two more sets of samples were drawn. After sampling, the SALADs were removed. However, just as an opportunity sample, PIC and Phosgene samples were taken from the area where the SALADs had been. Both showed non-detectable levels. The temperature while samples were collected was in the mid-80's. Also noted was a considerable degree of water condensation on the inner surface of the SALAD. So

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much condensation formed during the first hour and remained during the experiment, that the view into the SALAD was obscured, rendering the SALAD more translucent than transparent.

As presented in Table One, there appeared to be no detectable conversion of PIC into phosgene. This may be because insufficient ultraviolet light is penetrating the acrylic material of the SALAD. Or this may be related to some effect that the high relative humidity within the SALAD, either by moisture reacting with phosgene (or any of the intermediates during the conversion) or from the condensation reducing the ultraviolet penetration.

I propose further experimentation that controls more of the confounders, i.e. humidity, soil absorption, ultraviolet blockage, etc. Next summer, instead of placing them on untilled soil, we will place the SALADs on non-porous, plastic surfaces, to eliminate both soil absorption and a moisture source. If we detect phosgene under these conditions, we will continue with the proposed protocol for in-field use with agriculturally applied PIC. If there is no detection of phosgene, I would suggest we terminate any further SALAD experiments. However, when future PIC exposure monitoring studies are conducted, we could also run a few samplers for phosgene.

Related HSMs:

[HSM-13011](#) - Results From Sampling For Phosgene Using Salad Devices Positioned On Tarped Bedded Field Treated With Chloropicrin And 1,3-Dichloropropene

[HSM-13012](#) - Results From Sampling For Phosgene Using Salad Devices Charged With Chloropicrin And Positioned On Non-Absorbent Surface