Department of Toxic Substances Control

Edwin F. Lowry, Director
8800 Cal Center Drive
Sacramento, California 95826-3200

Winston H. Hickox
Agency Secretary
California Environmental
Protection Agency

Gray Davis
Governor

M E M O R A N D U M

TO: Dan Ziarkowski
Unit Chief
Drug Lab Remediation & Time Critical Removal Unit

FROM: Matthew Vona
Hazardous Substances Scientist

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SUBJECT: INITIAL EVALUATION OF EMISSION FROM METHAMPHETAMINE MANUFACTURING VIA THE EPHEDRINE/RED PHOSPHORUS/HYDRIODIC ACID METHOD.

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In our recent survey involving all 50 states, environmental health departments and related professionals were asked what types of methamphetamine labs they commonly encountered. Eighty-six percent of the respondents reported that they had encountered the Ephedrine/Red P/HI method[1]. For this reason we studied the off-gas and residual chemical contamination produced by these methamphetamine laboratories. The following discussion is a summary of this research to date.

The Ephedrine/Red P/HI method can produce contaminants including, but not limited to methamphetamine, 1,2-dimethyl-phenyl-aziridine, phenyl-2-propanone, 1-benzyl-methylnaphthalene, 1,3-dimethyl-2-phenylnaphthalene[2], iodine, hydrochloric acid, and hydriodic acid. While visibly contaminated surfaces can be easily removed, non-visible, contaminant residues or chemicals of concern (COC) can often remain undetected. In attempting to address this problem, some agencies have suggested the use of methamphetamine as an indicator compound. The Washington State Legislature has set lab cleanup standards such that methamphetamine levels must be less than or equal to 0.1 micrograms per 100 square centimeters[3]. Colorado currently references the Washington cleanup standard[4]. The Oregon Department of Human Resources has set a clean-up standard of 0.5 micrograms per square foot[5]. Here we attempted to determine how methamphetamine is likely to be distributed as compared to other contaminants.

In the Ephedrine/Red P/HI method of manufacture there are three major phases or reaction "stages." The first is the synthetic stage in which the pre-cursor (ephedrine) is combined with

iodine, red phosphorus, and water. These precursor chemicals will form hydriodic acid when combined, although, it is not uncommon for hydriodic acid to be added as a precursor chemical. This initial stage will be referred to as the "cook" stage. The heating and agitation which results from boiling the reaction mixture causes significant emissions to occur during the cook stage. It is this stage where phosphene gas, phenyl-2-propanone, iodine, di-methyl aziridine, and naphthalene by-products are emitted. Interestingly, methamphetamine was the only non-detected compound during the cook stage.

The second stage involves methamphetamine extraction from the reaction mixture into a non-polar solvent. This is commonly referred to as the "base-out" stage, because a strong base (e.g., Red Devil Lye) is added to the acidic reaction mixture produced in the first stage to convert methamphetamine into its base form. The strong base thereby drives the methamphetamine out of the aqueous solution and into a non-polar solvent (e.g., Coleman Fuel© or toluene). The second stage is highly exothermic because it involves adding a strong base (e.g., sodium hydroxide) to the highly acidic first stage. Therefore, significant heat and vapors are generated during this stage.

The third and final stage is typically referred to as the "salt-out" stage, which involves bubbling hydrogen chloride gas through the non-polar solvent from the "base-out" stage. It is during the third stage that the base form of methamphetamine is converted into its water soluble 'salt' form as methamphetamine hydrochloride (methamphetamine HCl). Methamphetamine HCl is precipitated out as whitish-tan crystals in final product form.

## Experiment One

Initially, we had qualitatively analyzed the off-gas and headspace of the reaction vessel during the cook stage using a Solid Phase Micro Extraction (SPME) device. SPME has been previously shown to detect methamphetamine in the headspace of solid-dosage samples[6]. When these techniques were employed to analyze the headspace of the cooking reaction mixture, iodine, phenyl-2-propanone, and naphthalene by-products were detected. Methamphetamine, however, was not detected. Subsequently, identical sections of building material were then passively exposed to the vapors from the cook, base-out, and salt-out stages. Swabs were taken, extracted, and analyzed for pH and chemical content using GC/MS.

**Figure 1. [LEFT] This is the setup where different surfaces were passively exposed to exhaust vapors created by an Ephedrine/RedP/HI manufacture operation. Note that the vent is located directly below all of the materials exposed creating a 'worse case' scenario. [RIGHT] This picture shows unexposed (left) and exposed (right) building material. The materials (clock-wise from the upper left hand side) are particle board with white plastic laminate, wall board, cedar, linoleum, sheet metal, and red brick. Note that portions of the galvanized sheet metal have been stripped of their protective coating.**

**Table 1. Results of pH samples taken before and after exposures to the cook stage vapors.**

| Material | Un-exposed Surface pH | Exposed-Surface pH |
|---|---|---|
| Cedar wood | **6** | **2-3** |
| Drywall | **7** | **3** |
| Particle Board & Laminate | **6** | **5** |
| Linoleum | **6-7** | **3** |
| Brick | **8** | **8** |
| Sheet Metal | **6-7** | **3** |

Residues of phenyl-2-propanone, hydriodic acid, iodine, and naphthalene by-products were detected on materials exposed to the cook-stage, while **no** methamphetamine was detected. Methamphetamine was detected, however, on those materials exposed to the headspace of both the base-out and salt-out stages (See Table 2).

Table 2

| Sample Description | Exposed to vapors above the "cook" stage | | Exposed to vapors above both "base-out" and "salt-out" stages. | |
|---|---|---|---|---|
| | Water swab | Chloroform swab | Water swab | Chloroform swab |
| **Particle board covered with laminate** | *NSD | NSD | Methamphetamine | Methamphetamine |
| **Linoleum tile** | NSD | NSD | Methamphetamine | Methamphetamine |
| **Cedar wood** | NSD | NSD | Methamphetamine<br>Indications† of Iodine | Methamphetamine<br>Indications of Iodine |
| **Red brick** | NSD | NSD | Methamphetamine | Indications of Methamphetamine |
| **Sheet metal** | Dichloroiodomethane | NSD | NSD | Methamphetamine |
| **Drywall** | Iodine was detected. | NSD | Methamphetamine<br>Indications of iodine. | NSD |

* No substances associated with methamphetamine manufacture were detected.

† Indications denote that, while the detected compound was present, it was of sufficiently low concentrations as to yield a partial spectrum.

**Figure 2. This (left) is the exposed cedar shown next to the residue left against white butcher paper after contact overnight. Wallboard (right) which has been exposed seems to take on the purple iodine color when compared to unexposed wallboard.**

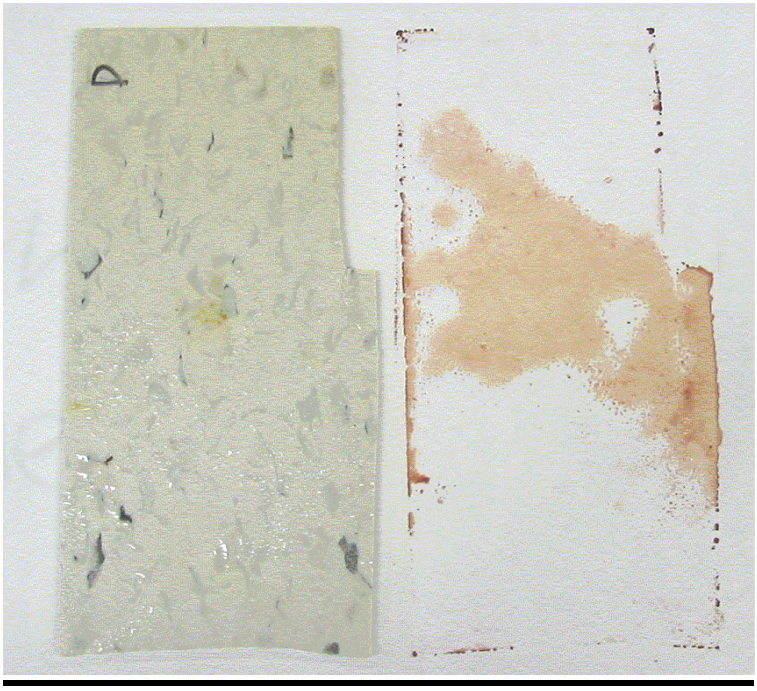

**Figure 3. The acidic vapors which condensed onto the linoleum reacted with butcher paper to leave this characteristic red staining. Note the blotches of yellow stain on the linoleum.**

A more thorough analysis of the off-gas coming from the cook and base-out stages of the Ephedrine/Red P/HI method was subsequently performed.

## Experiment Two

The emissions from two identical, Ephedrine/Red P/HI methamphetamine cooks were analyzed using active (vacuum) filtration of the vapors through a low-temperature, bi-layered liquid trap consisting of n-hexanes and de-ionized water. The vapors from both the cook and base-out stages were analyzed separately.

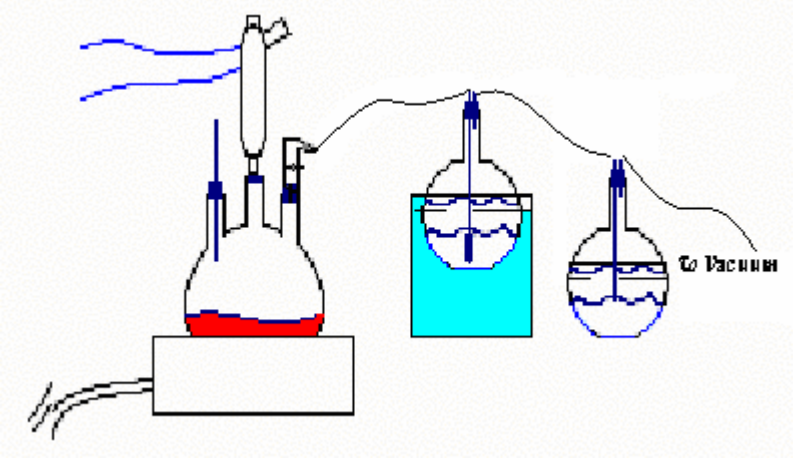


**Figure 4. This is a diagram of the bi-layered liquid trap setup. The vacuum was drawn from the headspace of Trap 02 (located furthest right in the above diagram). This under-pressure drew in the headspace of Trap 01 (located center) through a tube which was submerged beneath the bi-layer of water and n-hexanes in Trap 02. The under-pressure created in Trap 01 drew off the headspace from the reaction vessel (located furthest left) through a ground glass diffuser which was also submerged under the bi-layer of water and n-hexanes in Trap 01. Trap 01 was continually cooled using an ice-water filled beaker which was raised to submerge the trap. The triple necked reaction vessel had one thermometer, one reflux column (used as a precautionary measure), and a ground glass stop cock which was used to regulate the under pressure created in the reaction vessel.**

**Figure 5. This is a photograph of the actual laboratory set-up.**

The chemical contents of each layer in the traps were then qualitatively analyzed using Gas Chromatography / Mass Spectroscopy (GC/MS). Sub-samples were submitted for quantitative analysis. From the "cook" stage, methamphetamine, was not detected in the off-gas. Phenyl-2-propanone, iodine, and acids (assumed to be hydriodic acid) were detected in the off-gas from this stage. Though not chemically identified, red phosphorus also appeared to be present in the off-gas of the cook stage (See Figure 6).

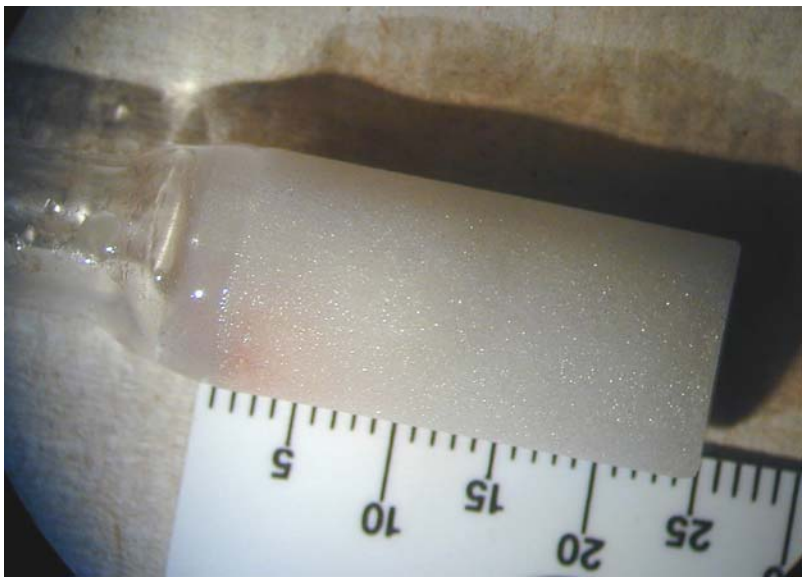


**Figure 6. A fine red powder (consistent with red phosphorus) was found to be trapped in the ground glass diffuser of Trap 01 during both cook stages. It is assumed that this came from particulate suspended in the vapors because there was never any liquid transfer from the reaction vessel into the vacuum line. The trapped powder diffused approximately 5mm into the ground glass diffuser indicating a very fine particle size.**

Methamphetamine was detected in the off-gas during the "base out" stage. Methamphetamine was primarily distributed into the organic phase of the bi-layer liquid trap which is indicative of methamphetamine contamination being present in the base form. None of the other contaminants or potential chemicals of concern, however, were detected.

If methamphetamine emissions occurred during all stages of methamphetamine manufacturing and could consistently be found with other COCs (e.g., iodine, phenyl-2-propanone, naphthalene by-products, and hydriodic acid), then it could serve as a suitable "indicator" chemical. Here, we observed that methamphetamine contamination was released in the base-out and/or salt-out phases of the cook, while phenyl-2-propanone, iodine, and other potential contaminants of concern were detected primarily in the off-gas from the cook stage. These results **preliminarily** contraindicate methamphetamine being used solely as an "indicator" chemical in assessing methamphetamine laboratory contamination for the Ephedrine/Red P/HI method of synthesis. However, the results do indicate that methamphetamine is a COC for this synthetic method.

We are waiting for results from a more sensitive quantitative analysis of the bi-layered liquid traps. It is expected that methamphetamine will be detected from all phases, albeit in much lower concentrations from the cook phase than from the base-out phase. This analysis shall be performed by the Department of Justice, Bureau of Forensic Services, Toxicology Laboratory. Subsequent to receiving these results, the above data and results will be formally documented.

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[1] A. Allen et al., "Synthetic Reductions in Clandestine Amphetamine and Methamphetamine Laboratories: A Review", Forensic Science International, 42, 183-199 (1989)

[2] S. Cantrell et. al., "A Study of Impurities Found in Methamphetamine Synthesized From Ephedrine" *Forensic Science International* 39, 39-53 (1988)

[3] Washington Administrative Code 246-205-541

[4] Michele Ames, "US CO: Danger of Meth Labs Lingers", Rocky Mountain News, Jan 29, 2003.

[5] Tom Mitchell in a Memo to "Licensed Drug Lab Cleanup Contractors" dated March 3m, 1999, not published.

[6] C. Koester et. Al., "Optimum methamphetamine profiling with sample preparation by solid-phase micro extraction", Journal of Forensic Sciences, 47, 1002-1007 (2002)