Chemicals in containers – problems and risks

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Chemicals in containers

The problem of hazardous chemicals in shipping containers has become a topic of major concern over the last 10 years. The combination of sealed containers and long journey times means that hazardous chemicals can build to a level that would never normally be encountered in domestic or industrial settings. The problem is exacerbated by the massive variety in chemicals involved, the origin of many containers in countries with less strict health and safety controls, and the often poor documentation accompanying the containers.

It has been estimated that about 15 percent of containers contain dangerous levels of chemicals, with about 0.5 percent presenting an immediate risk to health for workers at the receiving port. In the past, workers unaware of the risks have been exposed to these chemicals over long periods of time, and suffered health problems as a result, such as headaches, nausea, dizziness, and shortness of breath.

The chemicals involved are often odourless, and fall into two main categories: those used to fumigate the cargo in transit, and those emitted by the cargo itself. Fumigants initially received the greatest attention due to a couple of high profile cases of poisoning, but further large scale studies of containers have shown that chemicals from cargo are of equal, if not greater, concern.

Fumigants

Regulations laid out by the United Nations under ISPM15 stipulate that containers carrying certain types of materials (eg. wooded packaging and dunnage) should be fumigated to control the spread of pests and diseases. Although a relatively small percentage of containers are actually fumigated, those that are can present a serious health hazard, due to the toxicity of the chemicals involved, combined with the high levels needed for effective treatment. Alternatives to fumigation such as oxygen depletion and heat treatment are available, but may be more expensive or not appropriate for the type of cargo.

Thankfully, this situation is now starting to change in some countries at least, with ports routinely monitoring suspect containers, and passing on any costs associated with decontaminating the container back to the importer. Four main fumigants are of concern, though of course other pesticides may have been applied to foods before loading into the container. **Methyl bromide** was for a long time the fumigant of choice due to its ease of dispersion and effectiveness. However, it is also a potent ozone depletant and greenhouse gas, and is now banned in the European Union (EU), although it remains permitted for the treatment of solid wood packaging in ISPM15-compliant countries elsewhere. **Phosphine** is the major alternative to methyl bromide, and is typically supplied to the container as aluminium phosphide, a solid chemical that reacts with the water in the atmosphere to produce phosphine gas. In addition to gas remaining in the container upon arrival, the aluminium phosphide can fail to react completely during the voyage, leading to the production of large amounts of phosphine upon cleaning the container. **Sulfuryl fluoride** was little-used in the past, but appears to be undergoing a revival following the banning of methyl bromide. **Chloropicrin** is a pesticide in its own right, but is usually used with methyl bromide or sulfuryl fluoride to enhance effectiveness, and as a warning agent due to its pungent smell.

Chemicals emitted by the cargo

A massive variety of chemicals are used in the production of consumer goods, and over the past couple of decades releases of residual chemicals from products 'material emissions' has received increasing attention from the public and governments. In many countries, legislation is now coming into force that places the onus upon manufacturers to prove that their products do not emit harmful levels of chemicals, such as the Construction Products Regulation (CPR) in the EU.

Products intended for indoor use are of particular concern, especially with the rise of energy-efficient draught-proofed buildings with lower rates of air exchange that allow levels of chemicals to build up. Similar logic applies to the air in containers, but in this case the problem is multiplied by the large number of products often fresh off the production line, and therefore emitting high levels of chemicals.

Goods where glues or solvents are used in the manufacturing process are a particular concern, for example shoes and electronics. Chemicals of particular concern include low-boiling hydrocarbons such as benzene and toluene, and chlorinated solvents such as 1,2-dichloroethane. These are generally less acutely toxic to humans than fumigants, but can nevertheless be harmful. In particular, there is very little information on the hazards posed by long-term exposure to low levels of these chemicals, or on possible additive effects from simultaneous exposure to multiple chemicals.

What can be done?

Ports are already taking action on the above issues, with useful advice now available for port operators (see www.tgav.info). Actions include minimising the problem at source by reaching agreements with suppliers or importers, carrying out checks on containers deemed to be ‘at risk’, and educating port staff about the risks of opening containers and the signs of the presence of hazardous chemicals.

Despite these developments, it is likely that chemicals in containers will remain a hazard in a significant minority of containers for the foreseeable future, given the difficulties involved in implementing alternatives to fumigation and the ongoing issue of material emissions.

However, despite these complexities, there is one aspect that is straightforward – namely, the only way to be sure that a container is safe is to measure the chemicals inside it. But what’s the best way of doing this?

TD–GC–MS is widely recognised as the gold standard for analysis of gas samples.

Canister sampling in conjunction with thermal desorption is a powerful sample concentration technique for GC–MS.

Sorbent tubes are a convenient way of sampling vapours for analysis by TD–GC–MS.

Canisters complement sorbent tubes for analysis by TD–GC–MS by extending the range of compounds that can be detected.

Measuring chemicals

There are several methods to determine levels of chemicals in containers, and these range in cost and usefulness. Unfortunately, there is no perfect solution, so in many cases one or more of these methods will need to be applied.

Photo-ionisation detectors (PIDs) are handheld devices that provide a quick response for a limited number of chemicals, including methyl bromide and phosphine. However, they cannot detect chloropicrin, sulfuryl fluoride or 1,2-dichloroethane (amongst others), and are non-selective for hydrocarbons, so always need to be used in conjunction with other methods.

Gas detection tubes are glass tubes filled with a material that changes colour upon exposure to a particular chemical. The extent of the colour change provides a measure of the concentration of the chemical, but this is only approximate, and varies depending upon environmental conditions. Tubes are available for a range of the most commonly encountered chemicals.

Selective-ion flow-tube mass spectrometry (SIFT-MS) is emerging as the method of choice for rapid detection of fumigants from containers, as it is fast and provides a reasonably accurate indication of the amount of chemicals involved. Individual chemicals, on the whole, give distinctive 'signatures', and so comparison with a database allows identification. Detection limits have fallen in recent years, and are now well below those specified for human health. The equipment is relatively bulky, but can be housed in a mobile laboratory.

Thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS) is long-established and popular amongst analysts for detection of gases and vapours in a wide variety of situations. The air from the container is collected in a gas sampling bag, canister or sorbent tube, and then sent to a laboratory for analysis. Detection limits, as for SIFT-MS, are well below those prescribed, and massive libraries of data are available that allow identification and quantification of just about any chemical (although phosphine is tricky, and requires a modification to the analytical method). This makes it well-suited for the comprehensive analysis of materials – for example when dealing with new types of cargo or suspect containers, which may contain chemicals not present in a SIFT-MS library. The widespread use of GC–MS by analysts also makes it ideal for off-site confirmation of measurements, routine calibration of other methods, and research-level investigations, such as those into the efficacy of container ventilation prior to opening.

Container decontamination

With knowledge about the contents of the container in hand, the next step is simple at least in principle – ventilation to remove the chemical hazard. However, information remains limited about how effective this is, and if levels of chemicals are particularly high, then it may be necessary to take a second measurement after ventilation. In many cases, the levels of chemicals can be reduced to below the level that is hazardous to health, but in the case of material emissions, the problem may arise again when the product arrives at its final destination (eg. in someone's home). This issue of chemical emissions indoors is one that continues to receive a great deal of attention.

Conclusion

Eliminating hazardous chemicals at their source is clearly the ideal solution in any situation where risks to health are apparent. However, the complex networks of suppliers involved in the manufacture and supply of goods in the modern world mean that this option is not easy to apply to container shipping. Port managers therefore have to take the next-best option, that of reducing the risk to their staff as far as possible. This requires both constant awareness of the dangers, and a dedicated approach to monitoring levels of chemicals and taking the necessary action to decontaminate the cargo.

The difficulties involved in obtaining accurate and reliable information about the nature of the chemicals in containers – and the levels that are safe – means that it is wise to seek specialist advice on the best detection methods to use. Depending on the situation, multiple detection methods may be needed. For example, it is wise to regularly validate quick 'point-and-click' techniques with more robust methods.

The growing and widespread awareness of the dangers posed by hazardous chemicals at home and in the workplace will likely continue to drive the development of methods for detection of chemicals in containers. As well as engaging with suppliers to eliminate the problem at source, port managers would do well to consider the options for monitoring container air and minimising the risk to their workers by exposure to hazardous chemicals.

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ABOUT THE COMPANY

Markes International, headquartered in Llantrisant, South Wales, is a manufacturer of thermal desorption instruments, which concentrate trace-level chemicals in air or gas streams for detection by gas chromatography. Markes has been at the forefront of innovation in this field for 15 years, and is now involved in markets ranging from the monitoring of hazardous chemicals in urban air to ensuring compliance of consumer products with the increasingly strict regulations for chemical emissions. Markes' portfolio of products also includes numerous sampling accessories, and the widest range of consumables on the market.

BIOGRAPHY

Caroline Widdowson is a Material Emissions Specialist at Markes International. Her work involves focusing on industry emissions testing and the corresponding regulations and test methods. This includes collaborating with regulators and standards agencies around the world to create innovative and simple solutions for carrying out chemical emission tests.

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