# COUNTERFEIT REFRIGERANT IN FOOD TRANSPORTATION SEA CONTAINERS

AR LAWTON [a], N MARSHALL [b], P CLARKE [c]
[a, b] Cambridge Refrigeration Technology
140 Newmarket Road, Cambridge, CB5 8HE
Email: crt@crtech.co.uk, Fax: +44 1223 461522
[c] A P Moller Maersk
Esplanaden 50, 1098 Copenhagen K, Denmark

## ABSTRACT

During 2011 the compressors of a number of refrigerated shipping containers inexplicably exploded with the loss of life.

It was subsequently concluded that the cause of the explosions was counterfeit refrigerant that contained methyl chloride rather than a pure charge of the intended refrigerant HFC-134a.

This paper documents the ongoing investigation and describes the complex chemistry occurring within the refrigerant circuit that most likely caused the explosions and the methods proposed to eliminate the problem.

## 1.0 INTRODUCTION

On the 27th April 2011, at around 16:30, five people were seriously injured, two fatally, when the refrigeration unit of an empty shipping container inexplicably exploded at the terminal in Cat Lai, Vietnam. Around 17 hours later, at 09:15, on the 28th April 2011, a second container exploded. This explosion luckily caused no injuries.

Around the end of July 2011, a container was under repair in Oakland, US when spontaneous ignition of the refrigerant gas was noticed during a release of the gas to the atmosphere. The compressor was allowed to cool and the container isolated from the electrical supply. Again the gas was released and observed to ignite.

Another compressor later exploded in Brazil on the 7th October 2011. At the time of the explosion, the container was being serviced by an experienced technician on the third tier of a service area; he was fatally injured. The explosion completely destroyed the crankcase of the compressor, forcing it upwards and breaking the condenser coil in half. Debris was scattered around the front of the container and actually inside the container as the bulkhead was ruptured.

A further explosion occurred in China, this container was again a 40’ refrigerated container. The compressor exploded during a PTI on the 9th October 2011 in Qingdao Great Asia depot. Fortunately no one was injured as the technician was away collecting tools.

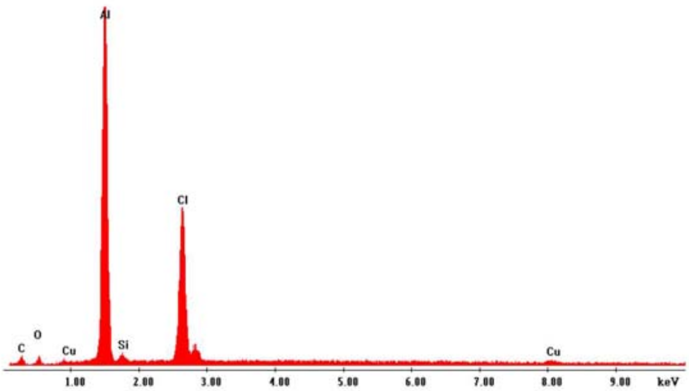
The explosions in Vietnam occurred in quick succession of each other, as did the explosions in Brazil and China. The common thread was that all these refrigerated containers appear to have passed through Cat Lai at around the same time as the explosions occurred there.

## 2.0 INVESTIGATION

After the first two explosions in quick succession, there was obviously much consternation within the industry as to their cause. The initial hypothesis of the local authorities was that the explosion was due to terrorism as the containers were at a quasi-military area, this was quickly ruled out by an explosive sampling swab which was negative.

Anther hypothesis was that the units had been accidentally pressure tested with oxygen rather than dry nitrogen or that the technicians had been leak testing with air or old refrigerant. According to volumetric calculations it is just possible to achieve an explosion under certain conditions of pressure and contamination. However, as there were explosions in quick succession it appeared unlikely that precisely the required conditions could occur simultaneously.

Samples taken from exploded compressor revealed an absence of metallic aluminium (no conrods or pistons) but the following energy-dispersive X-ray spectroscopy (EDX) spectrum indicating the strong presence of aluminium, chlorine and, surprisingly, some silicone.



SEM-EDX analysis spectrum from field EDX 1

**Figure 1 - EDX Spectrum Analysis**

The breakthrough occurred when a contaminated container was found that had not exploded. This refrigeration unit was observed to leak a transparent fluid, which smoked and caught fire in contact with air, which indicated the presence of an organo metallic compound. Samples of the refrigerant gas were taken and analysed by gas chromatography / mass spectrometry (GC/MS) and contained in addition to HFC-134a, methyl chloride, various hydrocarbons and tetramethylsilane. Also, the entire container was inverted and a sample of the oil was taken and subjected to GC/MS and also to analysis by nuclear magnetic resonance, (NMR) where Trimethyl aluminium was identified as shown below.

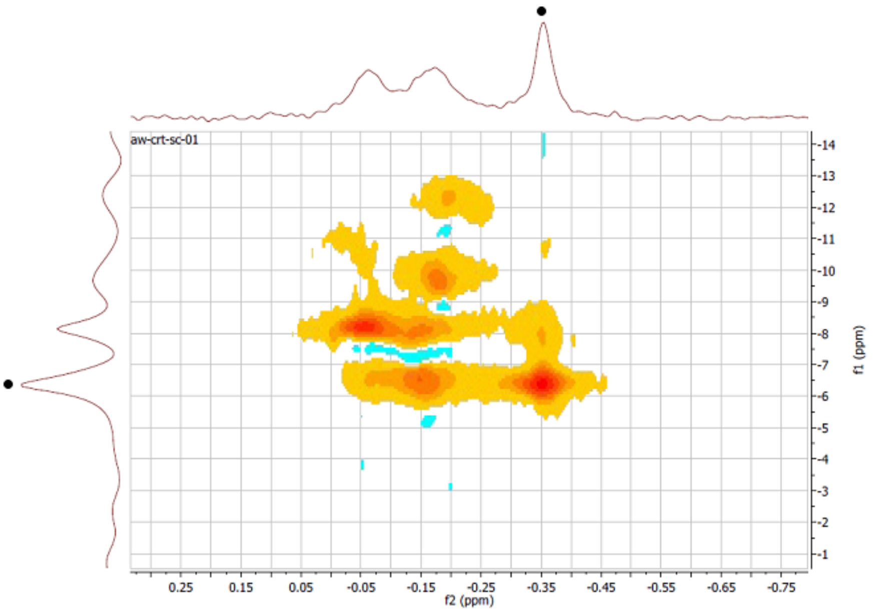


Figure 6 HSQC NMR spectrum of industrial aliquot 1, revealing at least three types of $AlCH_n$ ($n = 1, 3$) unit, including TMA (●). The analysis of a second industrial sample revealed essentially identical results

**Figure 2 NMR Spectrum Identifying TMA**

Refrigerant samples were also taken from other refrigeration units and their refrigerant contents analysed. It was subsequently confirmed that the cause was refrigerant contamination with methyl chloride, causing a pyrophoric compound called trimethyl aluminium to be formed by its attack on the aluminium components within the compressor.

## 3.0 CAUSE OF EXPLOSIONS

Many chemicals will burn in air if ignited by a flame, for example propane gas. However a bottle of compressed propane will not ignite if there is no air (oxygen) present. Some chemicals are so reactive that they ignite on contact with air (pyrophoric), for example the metal potassium. Explosives are different in that they contain their own source of oxygen and once triggered react without the presence of air, for example gunpowder combines charcoal and sulphur (which burn) and potassium nitrate (an oxidising agent).

A container charged in Vietnam had its gas contents analysed and was found to contain around 45% HFC-134a and almost 50% methyl chloride (R-40).

If R-40 were to be used in a system containing aluminium, as do modern refrigeration compressors, then it is possible that the aluminium would react with the R-40 at high temperatures (e.g. in the compressor cylinder head or at frictional surfaces of a compressor) to produce an alkyl-aluminium such as trimethyl aluminium. This reaction was reported by Walker and Wilson in a paper dated 1937 (ref. 5).

These alkyl aluminiums are likely to be pyrophoric and will rapidly decompose or ignite on contact with moist air to yield alumina (white smoke). These alkyl aluminiums can also react with other chemicals such as halocarbons (refrigerants) according to Wileys guide to chemical incompatibilities.

## 4.0 METHYL CHLORIDE (R-40)

Methyl chloride, or “chloromethane”, ASHRAE classification R-40 is a clear, colourless gas, formula $CH_3Cl$. Methyl chloride is a chemical compound of the group of organic compounds called haloalkanes. It has a faint, sweet odour that is noticeable only at levels that may be toxic; hence odorising agents are frequently added to it. It is heavier than air and extremely flammable. It is stored and shipped under pressure.

Clear, colourless gas
Flammable
Formula $CH_3Cl$
Density 0.75g/ml
Vapour pressure 3800 torr at 22°C
Similar to HFC-134a
Ionisation 11.4 EV

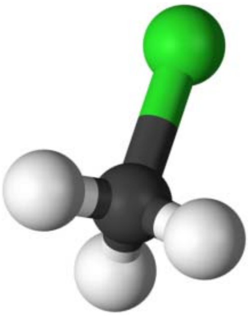


**Figure 3 - Methyl Chloride Properties**

Methyl chloride was frequently used as a refrigerant up until around 30 years ago but no longer, at least in the western world, due to it's toxicity and flammability. It is, however, still used in many other applications such as the production of silicone rubber and is widely available for purchase. If the temperature and pressure chart is studied it can be seen that it could easily be used as a substitute refrigerant for HFC-134a.

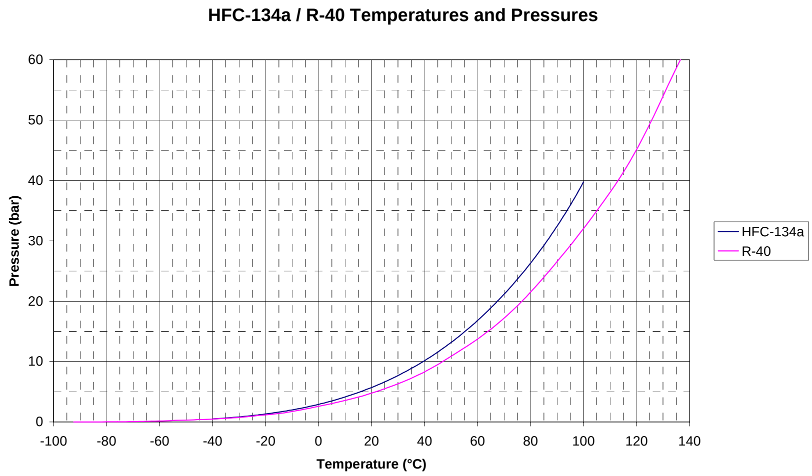


**Figure 4 - Pressure Temperature Relationship**

Methyl chloride slowly decomposes in the presence of water to form hydrogen chloride, which is corrosive to metals. Methyl chloride reacts explosively with lithium, sodium, potassium, and magnesium. The spontaneously flammable trimethyl aluminium is formed upon reaction of methyl chloride with aluminium in the presence of trace amounts of aluminium chloride.

## 4.0 DETECTION OF METHYL CHLORIDE

Several methods are commonly used for the detection and identification of gases; these are infrared spectroscopy, ionisation and gas chromatography, sometimes combined with mass spectroscopy. Another method is chemical identification by reaction and colour change,

Below, methods for detection of methyl chloride are discussed.

## 4.1 INFRARED SPECTROSCOPY

Commercial refrigerant analysers use infrared spectroscopy for identification of refrigerants. Methyl chloride is difficult to detect, as commercially available refrigerant analysers confuse it with HFC-134a. This is because the absorption spectra for these two gases overlap as shown below.

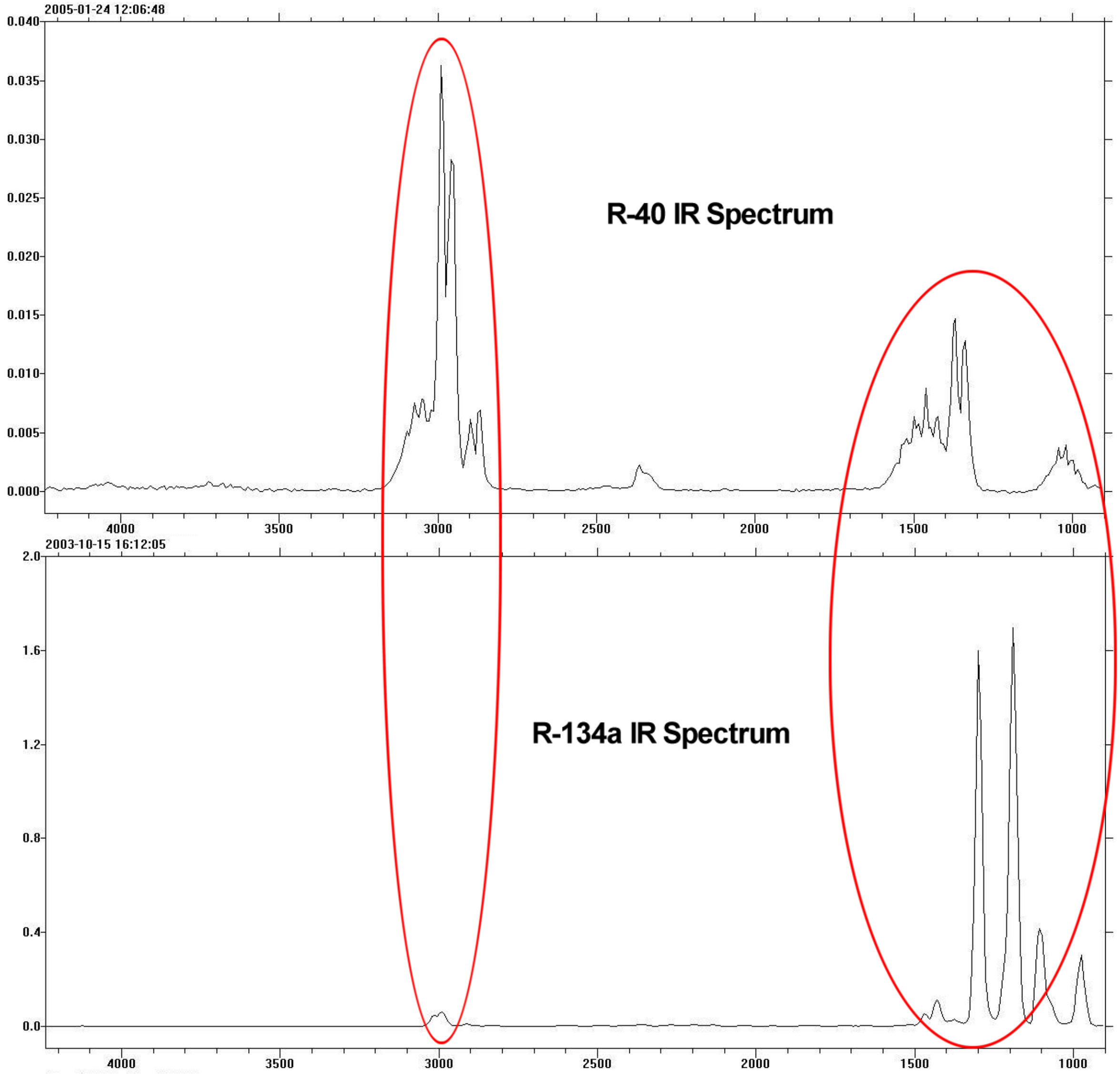


**Figure 5 - Absorption Spectra of HFC-134a and Methyl Chloride**

At least one major commercial analyser manufacturer has developed an analyser, which will identify chloromethane in a refrigerant mixture at a concentration of 3 to 5% as an unknown. While this is satisfactory for checking new refrigerant it is not for checking the existing refrigerant charge of a machine.

## 4.2 IONISATION

The ionisation of a gas by various means allows its irradiance to be measured with a suitable detector. Flammable organic compounds are commonly detected with a volatile organic compound detector (VOC), these ionise the gas under test with a high-energy bulb. Unfortunately most detectors have a 10.4 EV bulb whilst the ionisation potential of methyl chloride is 11.4 EV. Bulbs with an EV of 11.7 exist but have a short lifespan.

Another method using ionisation is to use a flame to ionise the gas and to react it on a copper plate causing a flame colour change to green.

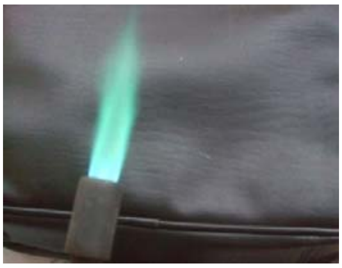


**Figure 6 - Flame Halide Test Showing Chlorine**

This is the previously used flame halide test for chlorine which used to be used for chlorinated refrigerants (ref. 7), and, should it be positive, it is followed by a GCMS test (gas chromatography/mass spectrometer) to check for the actual presence of chloromethane as described below.

## 4.3 CHEMICAL COLOUR CHANGE

Another commonly used method for gas detection is the so-called gas detector tube. In this case the tube uses a reaction between chlorine, released by the action of sulphuric acid and chromium trioxide, and o-tolidine to produce orthoquinone which has reddish orange colour.

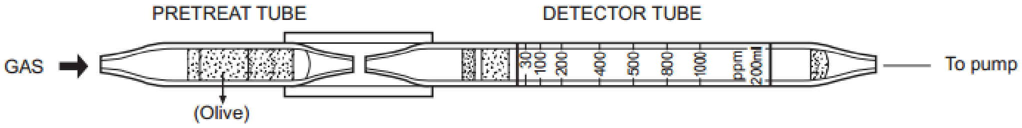


**Figure 7 - Gas Sample Tube**

Sensitivity is high, within the range 10-200ppm. Halogens and halogenated hydrocarbon cause interference and cross sensitivity; therefore this is not a specific test.

## 4.4 GAS CHROMATOGRAPHY MASS SPECTROMETRY

Gas Chromatography especially in conjunction with mass spectrometry can specifically identify methyl chloride.

Typically gas-chromatographic analysis is carried out with a GC-MS system with a mass sensitive detector using a 30m capillary column and sample injection via gas loop, the carrier gas is helium. A typical temperature programme used by the GC would be to start at a temperature of 40°C for 4 minutes followed by heating at a rate of 20K/min up to 240°C and finally and 6 minutes at 240°C.

A technical difficulty is that in the GC-MS analysis, HFC-134a and R-40 elute simultaneously so that both substances are not detectable as separated peaks. In cases of low concentrations of R-40, the amount of R-40 has to be determined after a calibration by analysing the peak area of the fragment.

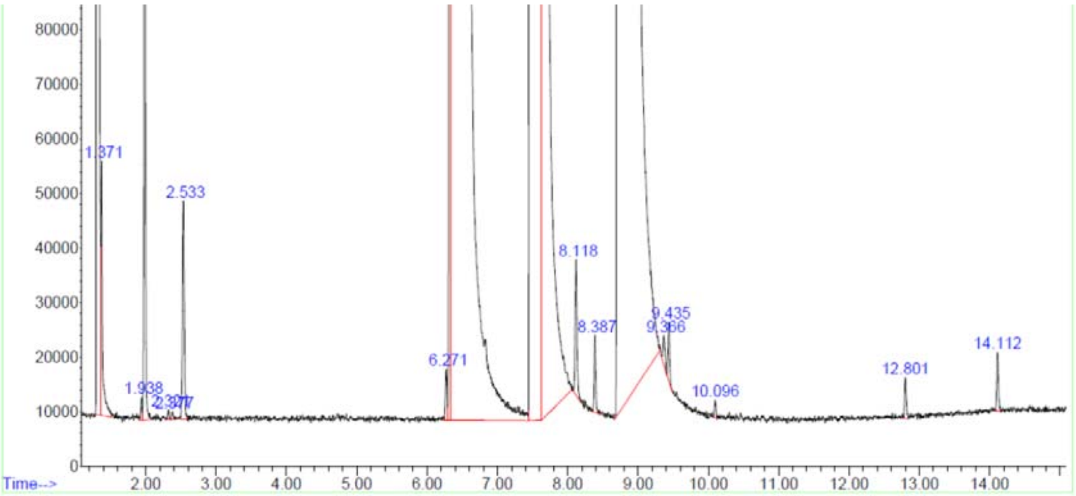


**Figure 8 - Example of GC Analysis**

Currently the best way to check for contamination is to check refrigerant samples using the flame halide torch or the gas detector tubes and if positive take a sample for GC/MS analysis.

## 5.0 TRIMETHYL ALUMINIUM

Trimethyl aluminium (TMA) exists as a dimer molecule with the formula $Al_2(CH_3)_6$ as the dative covalent bonds formed are energetically favourable than an arrangement with two separate molecules.

Below are some plausible stoichiometric reactions and products formed in the refrigeration system when methyl chloride is present.

| $6CH_3Cl$ | + | $4Al$ | $\rightarrow$ | $Al_2(CH_3)_6$ | + | $2AlCl_3$ |
|---|---|---|---|---|---|---|
| methyl chloride (R-40) | | aluminium | | trimethyl aluminium | | aluminium chloride |

Trimethyl aluminium is a powerful reducing agent and reacts violently with the following: oxidisers, alcohols, amines, amides, inorganic hydroxides, carbon dioxide, carbon tetrachloride, halon, halogens and halogenated hydrocarbons, oxides of nitrogen or sulphur, phenols, triethylborane, and many other substances.

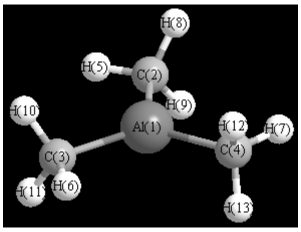


**Figure 9 - Trimethyl Aluminium Properties**

Trimethyl aluminium is a liquid at room temperature, melting at 15°C. It is, as already described, a dimer and is pyrophoric, combusting spontaneously with contact with air. The probable reaction is as follows:

| $Al_2(CH_3)_6$ | + | $24O_2$ | $\rightarrow$ | $AL_2O_3$ | + | $6CO_2$ | + | $9H_20$ |
|---|---|---|---|---|---|---|---|---|
| trimethyl aluminium | | air | | aluminium oxide | | carbon dioxide | | water |

The product of combustion in air is alumina, which is a white powder. Other reactions are possible, as detailed above, notably the reaction with halogenated hydrocarbons, which are, in fact, refrigerants such as HFC-134a.

## 6.0 TETRA METHYL SILANE

Tetra methyl silane (TMS) has been detected during analysis of some gas samples and also in the oil sample. The silicone detected in the EDX scan is believed to be a deliberate impurity of aluminium for machining purposes at a level of up to 10% by weight. TMS is probably formed either by direct reaction with chloromethane or by TMA alkylation. TMS reacts with air to form silicone dioxide (white smoke, in fact quartz). Alkylation is a possible route for the formation of TMS since, when TMS is found, other products such as isobutane and propanes are also often present.

# 7.0 SYNTHETIC POLYOL ESTER RL32H

Other than the refrigerant the other significant chemical in the refrigeration circuit is the oil, which is of a chemical group called a polyolester. As this is synthesised from alcohol and acid to produce this modified ester, there are at least two possible reaction possibilities. Direct reaction with the methyl chloride or possibly alkylation by TMA.

TMA (2.0 M in toluene) was added to synthetic polyol ester RL32H in toluene (20 ml distilled off Na) under $N_2$ and stirred at room temperature. Aliquots were analysed by NMR spectroscopy after 3 and 7 days. After 3 days incomplete reaction can be detected, with no significant changes detected thereafter. NMR spectroscopy reveals a clear highfield signal due to unreacted TMA and splitting of the δ4.22ppm multiplet into three clear signals in the range δ4.3-3.8ppm. A very minor singlet develops at δ3.12ppm attributable to OMe, but fails to grow significantly.

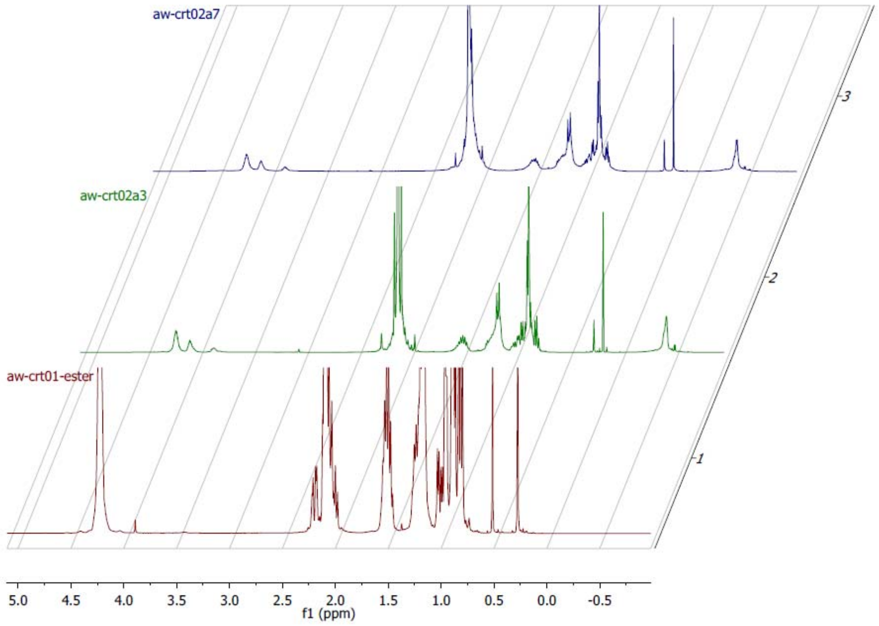


**Figure 10 - NMR spectra of RL32H (red) and after treatment with 1 eq. TMA (3 d green, 7 d blue).**

Unreacted TMA is clearly visible in the latter two spectra at very highfield. The isolated multiplet at d 4.22ppm is rapidly split into three signals (circled) indicating there was no significant reaction path.

Field examination has found either a black coke in the sump of compressors, which EDX shows to contain chlorine and aluminium, or sometimes a water-soluble brown sludge. In conjunction with the above this appears to indicate degradation of the polyolester oil by the methyl chloride back to acids and alcohols.

# 8.0 REFRIGERANT REACTION WITH TMA

One possible cause of the explosions has been hypothesised as the reaction of TMA with HFC-134a, potentially forming an expanding gas such as hydrofluoric acid (HF) or hydrochloric acid. A stream of HFC-134a was bubbled through TMA (2.0 M in toluene) added to synthetic polyol ester RL32H under $N_2$ and stirred at room temperature.

No reaction was observed, though other factors may be required to initiate it such as heat friction or other reagents.

## 9.0 REFRIGERANT CONTAMINATION WITHIN POPULATION

We have subjected in the region of 300 refrigerated containers to refrigerant halide flame tests and laboratory tests. The findings, where the intended refrigerant was not HFC-404a, approximate to the following:

**Table 1 - Contamination Percentages**

| | | | |
|---|---|---|---|
| Failed Flame Test: | 31% | Min R-40 Found: | 0.02% |
| Passed Flame Test: | 69% | Containing R-40: | 15% |
| Containing > 99.5% HFC-134a: | 71% | Containing > 0.5% R-40: | 7% |
| Max R-40 Found: | 41% | | |

Note that the lower limit for detection of an individual refrigerant is 0.015%. Contaminant HFC's were found in a number of cases in the laboratory reports. Whilst this would not trigger a fail of the flame test, being non-chlorinated, it was found that in cases where such fluorinated refrigerants were present, chlorinated gases were always present which would trigger a fail.

## 10.0 ELIMINATION OF THE PROBLEM

Within Europe, due to F-gas legislation, refrigerant is distributed in returnable bottles through major distribution networks; therefore there have been no known incidences of counterfeit refrigerants found containing methyl chloride. However, there are still instances of unbranded HFC-134a in illegal disposable bottles being present in the market. Up until now the major contaminant detected has been hydrocarbons which, though still dangerous, less so than methyl chloride.

Worldwide, F-gas regulations do not apply and so disposable bottles are in the majority and therefore extreme caution needs to be exercised, even refillable bottles have been found to be contaminated as they have been filled by third parties. From experience, the only way to eliminate the problem is to check each bottle with a flame halide torch as even certificates have been found to be counterfeit.

Work is currently ongoing to determine the best methods for eliminating contamination from existing machinery and recycled refrigerant. The problem being that it is difficult to be certain of the start concentration if reactions have proceeded. Where TMA is present it can be safely pacified by reaction with higher alcohols, though initial investigation have found difficulties with sludges and high acid levels.

## 11.0 CONCLUSION

This paper has described how the nature of the contaminated refrigerant was found to be methyl chloride and also how the reaction product trimethyl aluminium was identified.

In-service units can be tested for the chlorinated contaminants by use of the halide torch test. If found to be positive, they can then be tested by a gas chromatograph for the presence of methyl chloride. Should methyl chloride be detected, the units should be withdrawn from service. All refrigerant used for maintenance purposes should also be routinely tested.

The next research steps are to investigate the methods of reaction and find a simple test for differentiating between methyl chloride and other chlorinated gases.

It is clear that further work will be required to find ways of ensuring a clean supply chain of fluorinated refrigerants both new and recycled refrigerant and also a way of decontaminating the existing fleet of containers.

# 12.0 REFERENCES

1. Heap RD and Lawton AR, 1995, Developments in Container Refrigeration, *International Congress Of Refrigeration*, 2007, The Hague
2. International Standard ISO 1496-2 Series 1 Freight Containers - Specification and testing Part 2: Thermal containers
3. Technical Note 180S Sabre Kitagawa tubes
4. Andrew Wheatley Dr. Phil Harford PhD, 2012, Report No.2 Investigation of the composition and reactivity of counterfeit refrigerant (Private correspondence); Chemistry Department Cambridge University
5. Walter O Walker and Karl S Wilson, August 1937, The Action of Methyl Chloride on Aluminium, Research Department, *Ansul Chemical Company Murinette*, Wise
6. Wiley’s Guide to Chemical Incompatibilities, 2009, Trimethylalane or Trimethylaluminum (75-24-1) (Ch3)
7. Maersk Line, 16th December 2011, Technical Bulletin, Halide Torch Information.
8. Lawton and Cavalier, 2012, Risk Inherent in the Use of Counterfeit Refrigerants, *23rd Informatory Note on Refrigeration Technologies*, IIR, November 2012.