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# Detection of ambient explosive vapors at concentrations below parts per quadrillion

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LUX ET VERITAS

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# CONCLUSIONS on ACES

• **Product**: Air Cargo Explosives Screener (ACES), able to screen explosives while cargo is in "bulk" form, in particular complete trucks at the airport entrance,

• **Technology**: Explosives Vapour Detection (EVD) based on the integration of Differential Thermal Desorbtion (DTD), Secondary Electro Spray Ionization (SESI), Differential Mobility Analysis (DMA), and API Tandem Mass Spectrometry (API MS/MS),

•**Advantages**: ACES accomplishes two simultaneous goals: **increase security** through a higher PoD than current technologies, and **reduce screening costs and delays** to values well below present operations,

• **Development stage**: Equipment in the certification process in EU Nations,

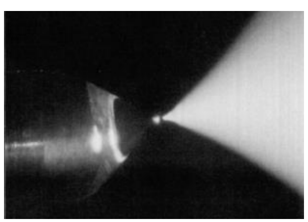
• **Present performance**: Minimum RDX detectable alarm: 0.03 ppq (parts per quadrillion), equal to $3 \cdot 10^{-17}$ atm,

•**Company**: SEADM, Morpho and CARTIF created in 2008 a Joint venture (SEDET), aimed at development of explosive detection equipments.

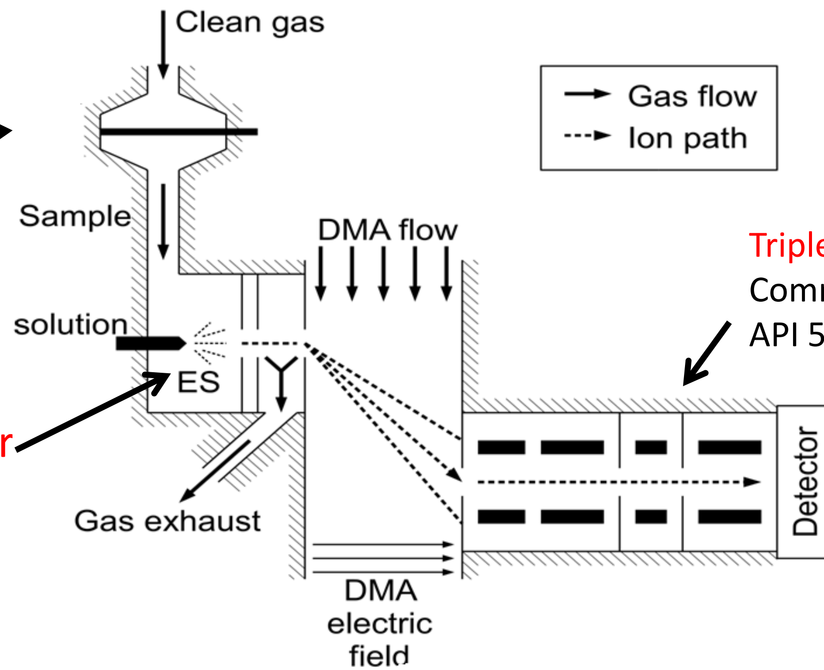
# Phenomenology being exploited for explosive detection

- Direct ambient vapor detection (Sniffing) via sampling, desorbing, ionizing ambient vapor, analyzing via ion Mobility and triple quad mass filters in series
- Focusing on Air Cargo Explosives Screener (ACES), ***sniffing*** the cargo bay by sampling ~1 $m^3$ of cargo air into a filter, and desorbing the filter into a suitable MS detector

Desorber



Ionizer




Triple quadrupole MS
Commercial: Sciex 's
API 5500: 3.4 lpm sample flow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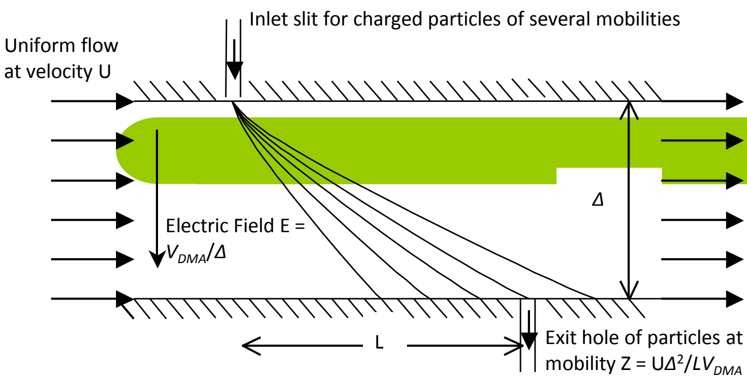
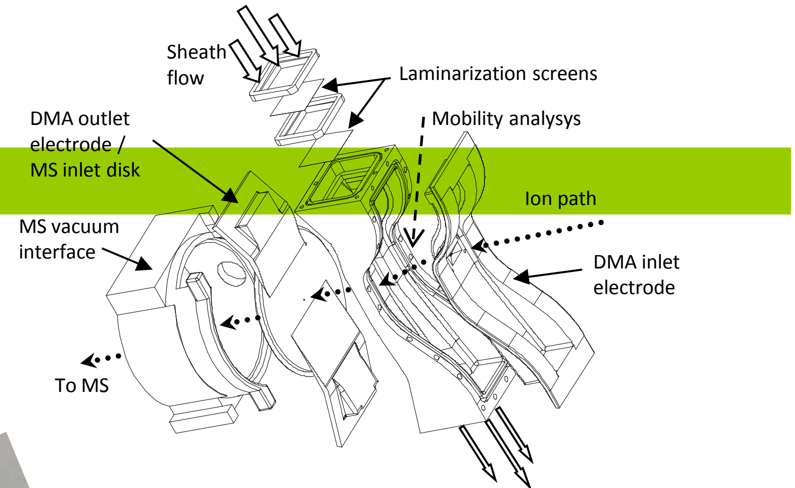
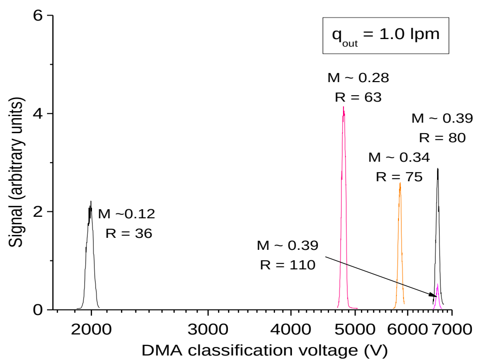
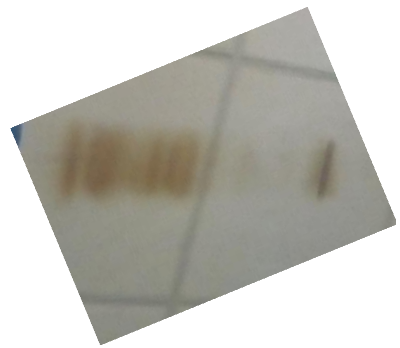
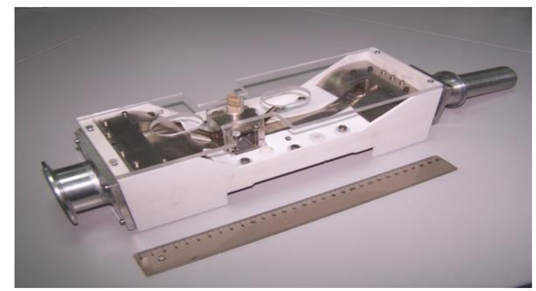
# Mobility filter: DMA (Differential mobility analyzer)





- One more narrow band filter added in series to triple quadrupole: Same sensitivity and measurement speed, but 10-100 increase in resolution
- Resolution: 50-100; transmission >50%
- Since ions need to be formed at atmospheric pressure, they may as well be used in mobility separation for greater resolving power. DMA may be viewed as a fast ion chromatograph substituting slower conventional chromatographies (LC or GC).
- DMA Developed at SEADM. No alternative true mobility separation device coupled commercially to MS available

*Fernández de la Mora et al. US patent 7,855,360, December 2010.*

*Rus et al. IMS-MS coupling a DMA to commercial API-MS systems, Int. J. Mass Spectrom,* ***298****, 30,2010*

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# Advantages of ambient vapor detection

- Sampling vapors directly from the atmosphere. No need for swabbing. No reliance on *particle events* of low probability.
- High Sensitivity (sub part per quadrillion) and specificity (low false alarm), both rapidly improving as technology develops and experience accumulates
- No alternative TSA approved method exists to **monitor the whole cargo as a unit**, without going through the lengthy and disruptive process of undoing the load and checking the packages one by one.
- Low global cost, fast analysis associated to **whole cargo monitoring, even when relying on a sophisticated detector**
- Minimizing delays and enabling 100% monitoring of all aerial cargo

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# ACES SOLUTION

SEDET has developed an explosive screener for air cargo (ACES), whose aim is to solve problems generated by present legislation, present screening costs, and state-of-the-art technologies.

ACES delivers a radical improvement from present explosive screening procedures:

- 100% of air cargo is inspected at the airport entrance,
- Screening is done directly on the truck prior to discharge,
- Screening is completed in a single operation in a few minutes,
- Screenings costs are many times lower than present-day operations,
- PoD and FAR improve considerably over present day performances.

# Sensitivity issues

- Broad perception that explosive detection by sniffing is not viable. YET
- Antecedents on measuring very low vapor concentrations (sub parts per trillion in 2009). Other groups are now (2013) reporting comparable results
- Sub ppq (<$10^{-15}$ atmospheres) in 2012
- Current: 0.03 ppq for RDX
- Is this enough?
- Can it be improved by orders of magnitude?

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# Prior work: (ASMS conference, 2009 )

## 20 ppq in direct ambient sampling

**SESI DETECTION OF EXPLOSIVE VAPORS BELOW 20 ppq ON A TRIPLE QUADRUPOLE WITH AN ATMOSPHERIC PRESSURE SOURCE;** E. Mesonero; JA. Sillero; M Hernández; Juan Fernandez de La Mora

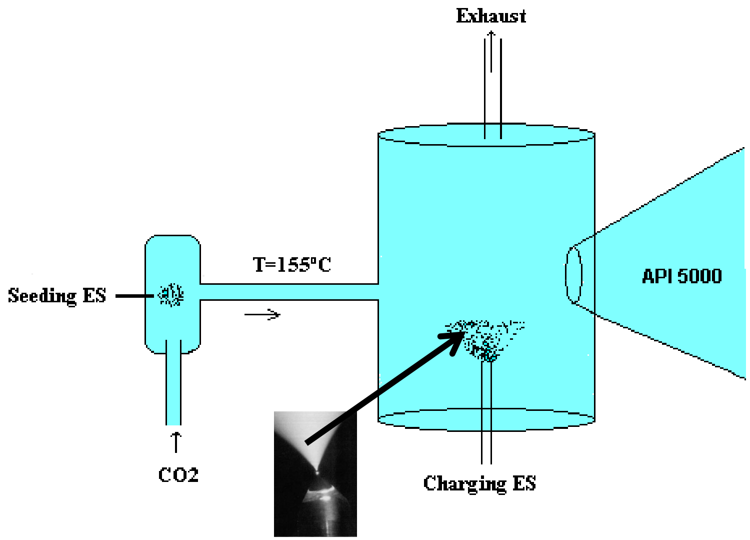
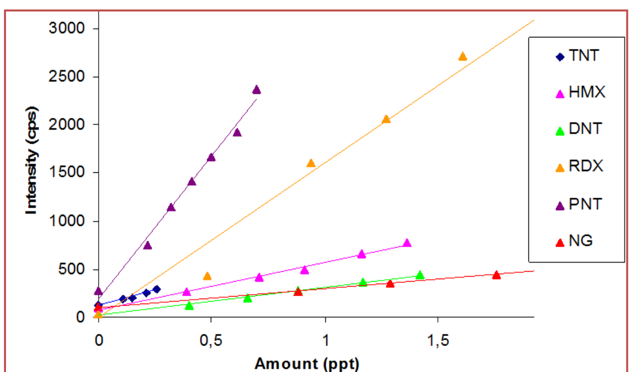



Table 1:Transitions for Explosives Detection

| Explosive | Precursor Ion (m/z) ⇨ | Product Ion (m/z) |
|---|---|---|
| TNT | 226.1 $(M-H)^-$ | 46.1 $(NO_2^-)$ |
| HMX | 340.9 $(M+HCOO^-)^-$ | 45.9 $(NO_2^-)$ |
| DNT | 180.9 $(M-H)^-$ | 45.9 $(NO_2^-)$ |
| RDX | 267.0 $(M+HCOO^-)^-$ | 46.0 $(NO_2^-)$ |
| PENT | 360.8 $(M+HCOO^-)^-$ | 62.1 $(NO_3^-)$ |
| NG | 271.9 $(M+HCOO^-)^-$ | 62.1 $(NO_3^-)$ |

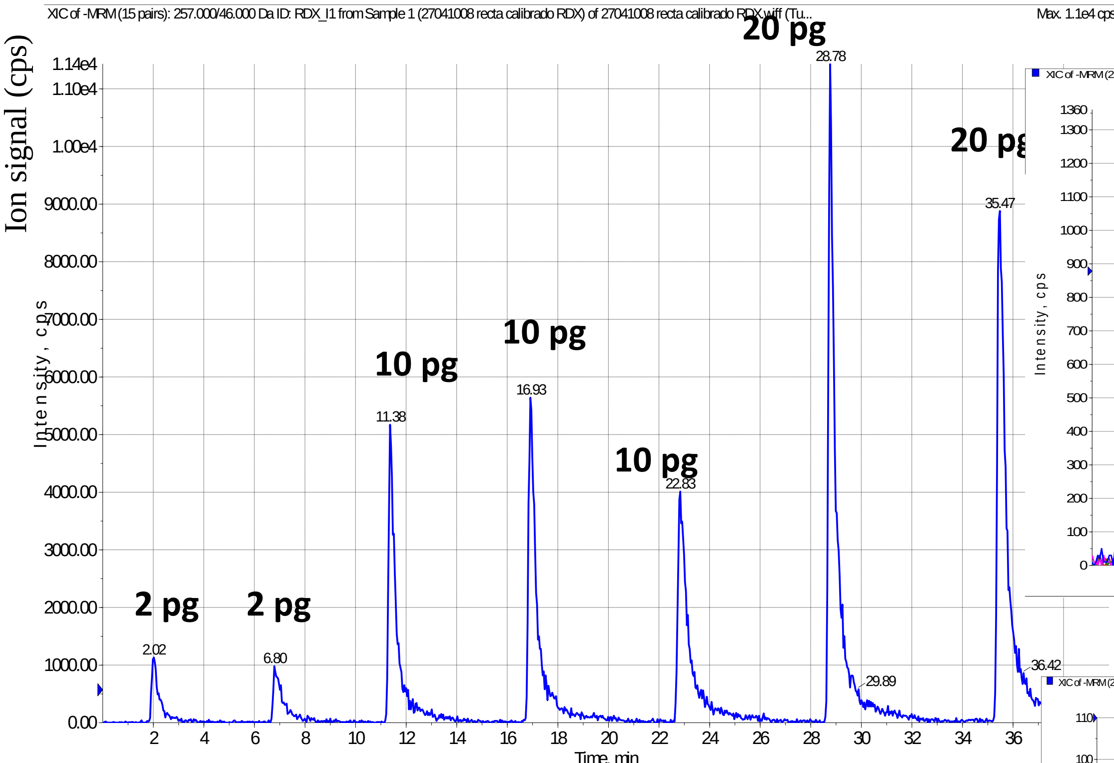
Background from clean air ~ 40-100 counts/s

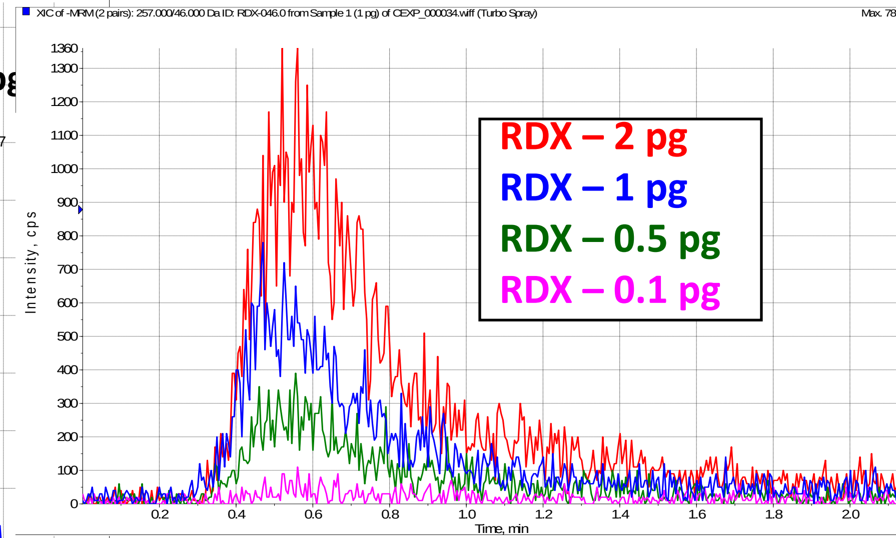


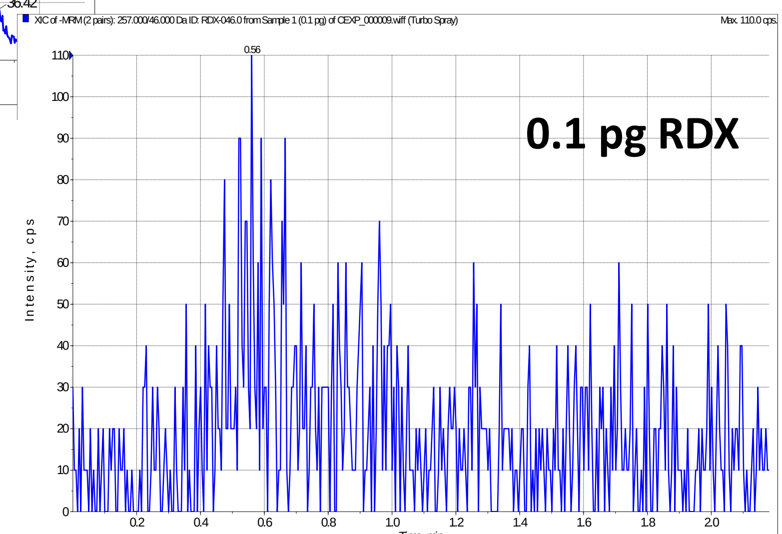

| Explosive | Sensitivity (ion/s/ppt) | LDL (ppt) IUPAC[1] | LDL (ppt) B-99%[2] |
|---|---|---|---|
| TNT | 633 | 0.07 | 0.018 |
| HMX | 494 | 0.11 | 0.025 |
| DNT | 295 | 0.12 | 0.023 |
| RDX | 1642 | 0.07 | 0.005 |
| PENT | 2959 | 0.04 | 0.006 |
| NG | 197 | 0.22 | 0.056 |

# RDX Calibration by desorbing sample deposited on filter

(Gordon Conference, 2012)

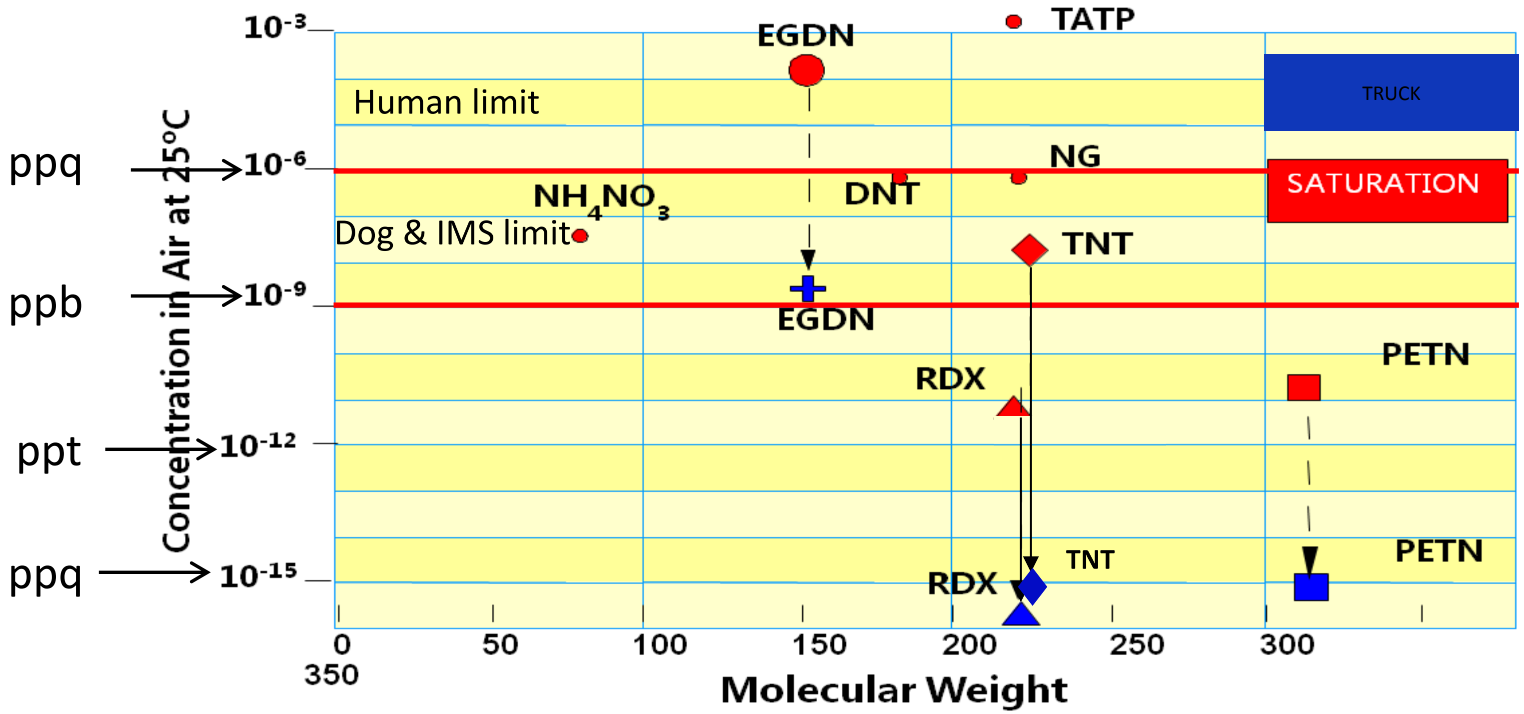


# Required sensitivity

SEDET tests (to be later discussed) show that explosives hidden in volumes up to 110 $m^3$ generate vapour pressures which are from $10^4$ to $10^7$ lower than the saturation value. Taking into account equilibrium vapour pressure of RDX, an effective Vapour Screener requires a sensitivity of 0.01 ppq.



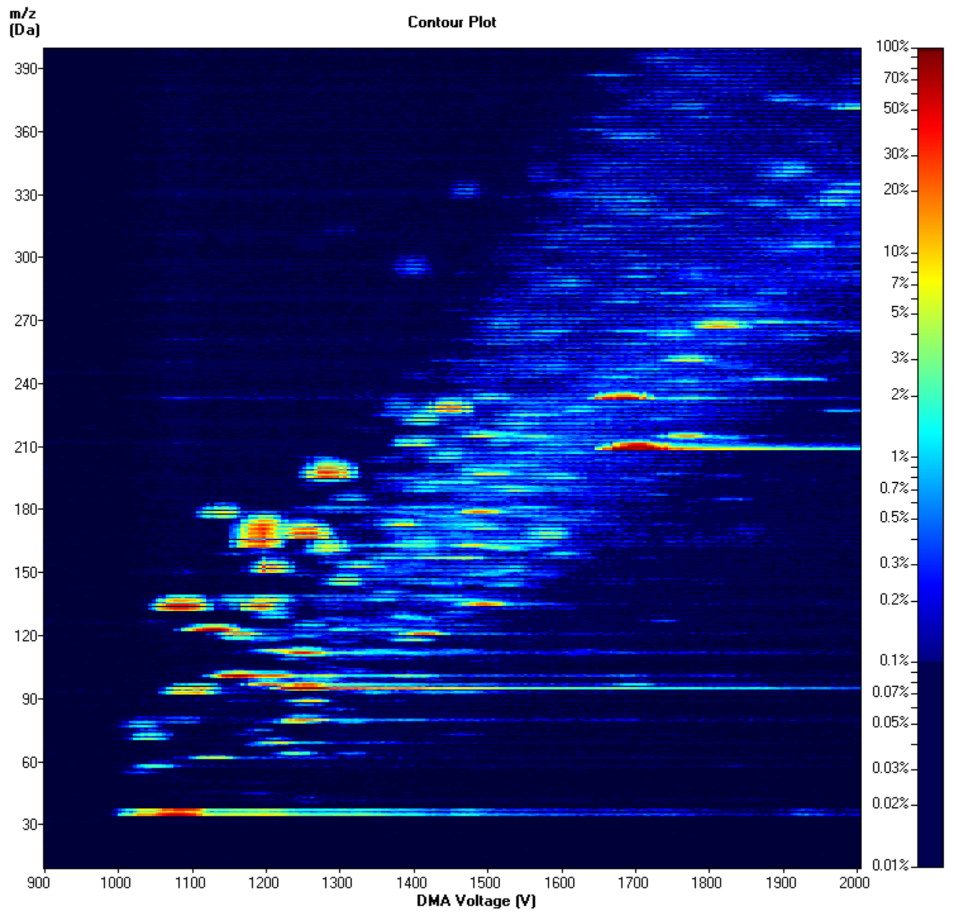
# Vapor sensitivity of contemperary triple quadrupole MS

- 1000 lit atmospheric air ~ $2.7\ 10^{25}$ molecules
- 0.001ppq ($10^{-18}$ atmospheres) in that air volume ~ $2.7\ 10^{7}$ molecules. **This is a very large number**
- Even allowing for limitations of sampling (10% vapor capture efficiency in collector filter), vapor ionization efficiency (0.1%) current triple quadrupole MS performance, (1% ion transmission and detection efficiency in MS), still 27 counts!
- Therefore, 0.001-0.01 ppq should be detectable today!
- NO SENSITIVITY PROBLEM at this concentration level

# False alarms: The resolution problem

- The real challenge is background noise from zillions of competing species in the atmospheric background. The larger the sensitivity, the greater the number of species with the same mass and the same primary fragment masses as the explosive monitored.

- Our approach to deal with this challenge is the use of multiple ion filters in series, all having relatively high transmission and resolution, all shifting in synchrony from one explosive to the next:
- Mobility filter (DMA)→triple quadrupole filter
- Substantial effort needs to be invested in minimizing internal noise and multiple sources of contamination.



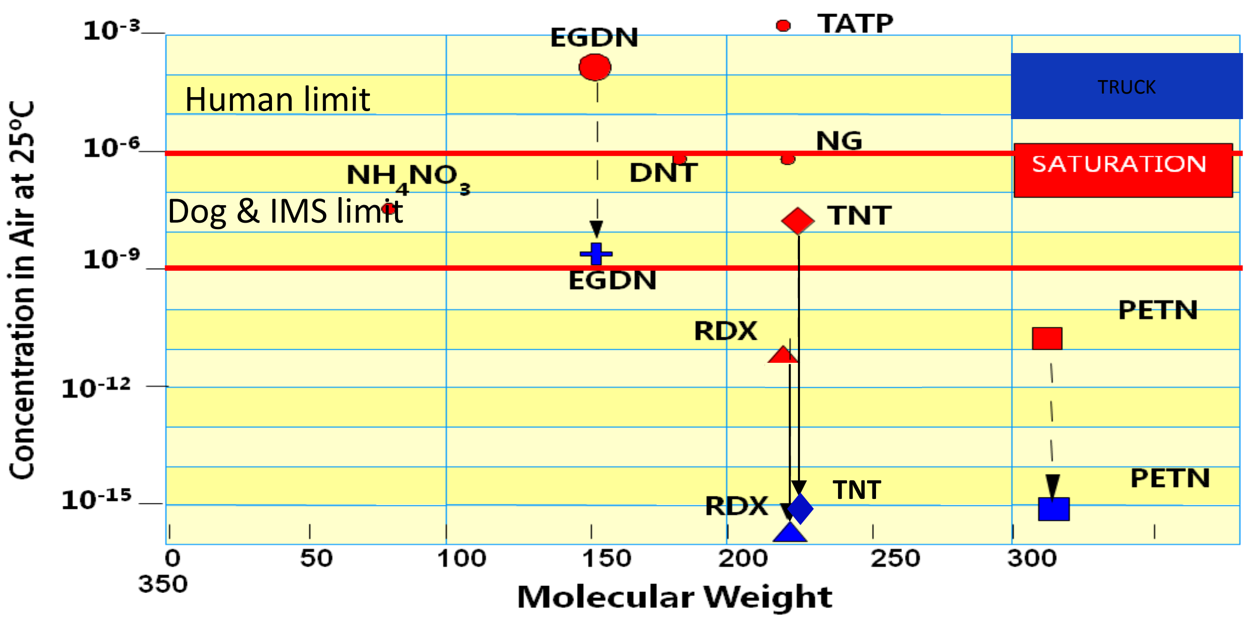
# • Operations

Cargo→Sample gas → vapors trapped in filter


vapors desorbed from filter → ionization (SESI)→ analyzer (Ion mobility filter+triple quad MS filter)

**Limitations based on concealment, containment, explosive type, minimum mass and other factors: A study of the dilution effect in real cargo loads**

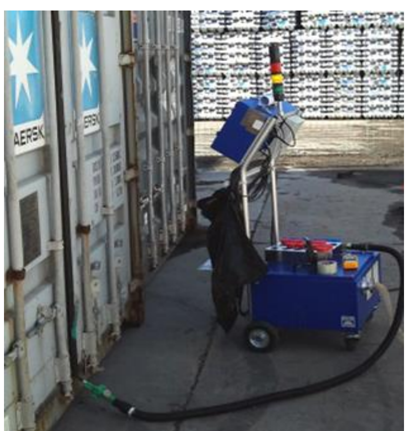
Our sensitive instrument permits detecting small masses of explosives hidden in cargo loads under a broad range of operational conditions. A large experience has been gathered in precertification tests in the UK the Netherlands, Germany, France and Spain. **The data to be discussed today have been obtained in the port of Vigo (NW Spain) in collaboration with the Spanish Guardia Civil**. The information to be presented is unique.



Dilution effects for vapor signal

The dilution effect: $p_v/p_{eq}(T)$, is a function of the following variables

1. Truck cargo bay volume,
2. Explosive confinement (packaging),
3. Cargo itself (stuff inside boxes),
4. Temperature,
5. Soaking time,
6. Distance from the explosive to the sampling point,



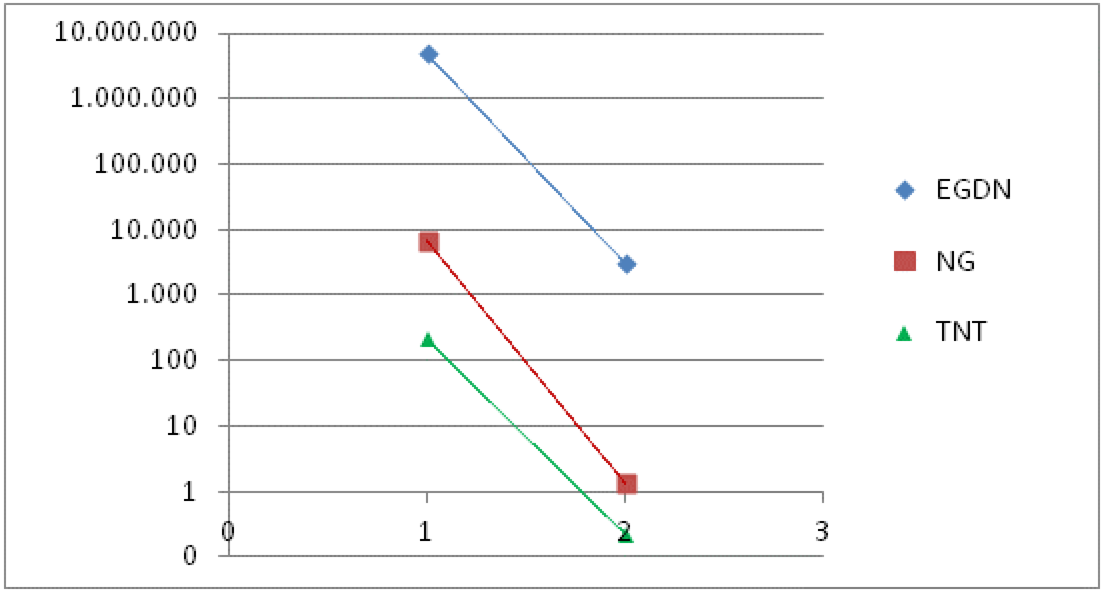
# Container or truck volume

| Volume effect | EGDN | Nitroglycerin | TNT |
|---|---|---|---|
| Saturation pressure (ppq) | $10^{11}$ | $10^{9}$ | $10^{6}$ |
| Partial pressure in 76 $m^3$ truck (ppq) | $5\ 10^{5}$ | 250 | 50 |
| Dilution factor | $2\ 10^{4}$ | $4\ 10^{6}$ | $2\ 10^{4}$ |

The vapor's partial pressure within a large volume such as a truck cargo bay is typically well below saturation. For EGDN and TNT, the dilution is ~ 20,000.

# Concealment effect

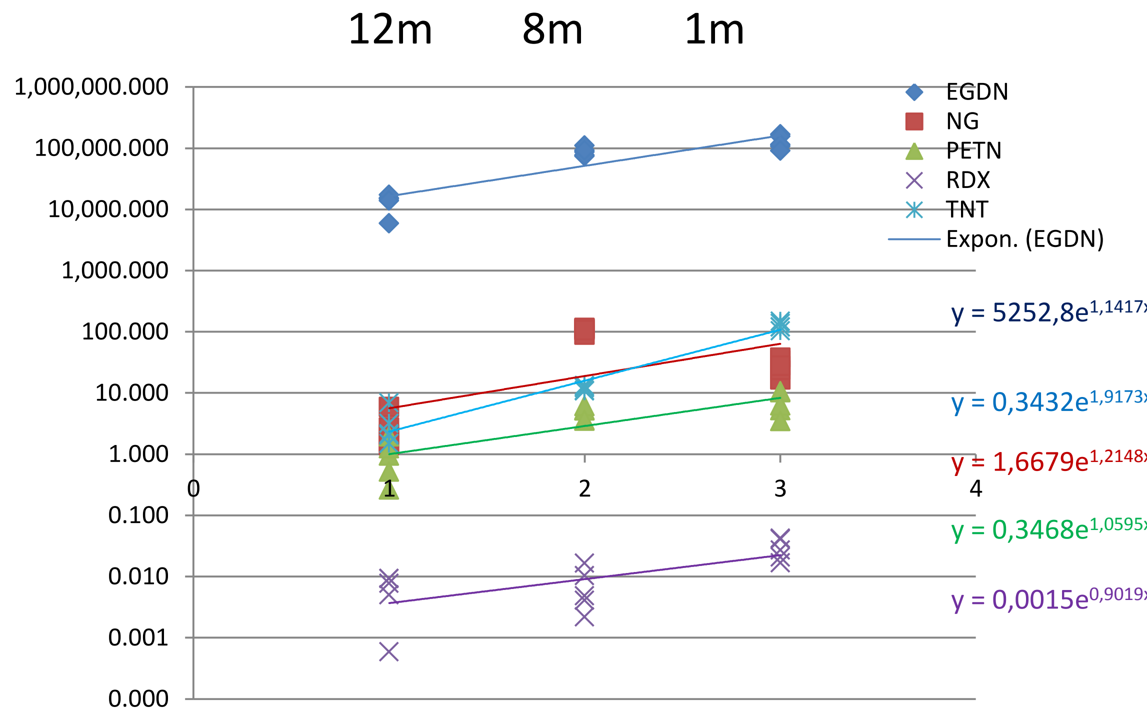
Explosive confinement in a carefully sealed box reduces vapor pressure by a factor of 1,000




EGDN, NG and TNT vapour pressure. Point 1 shows an open box, and point 2 shows a sealed box

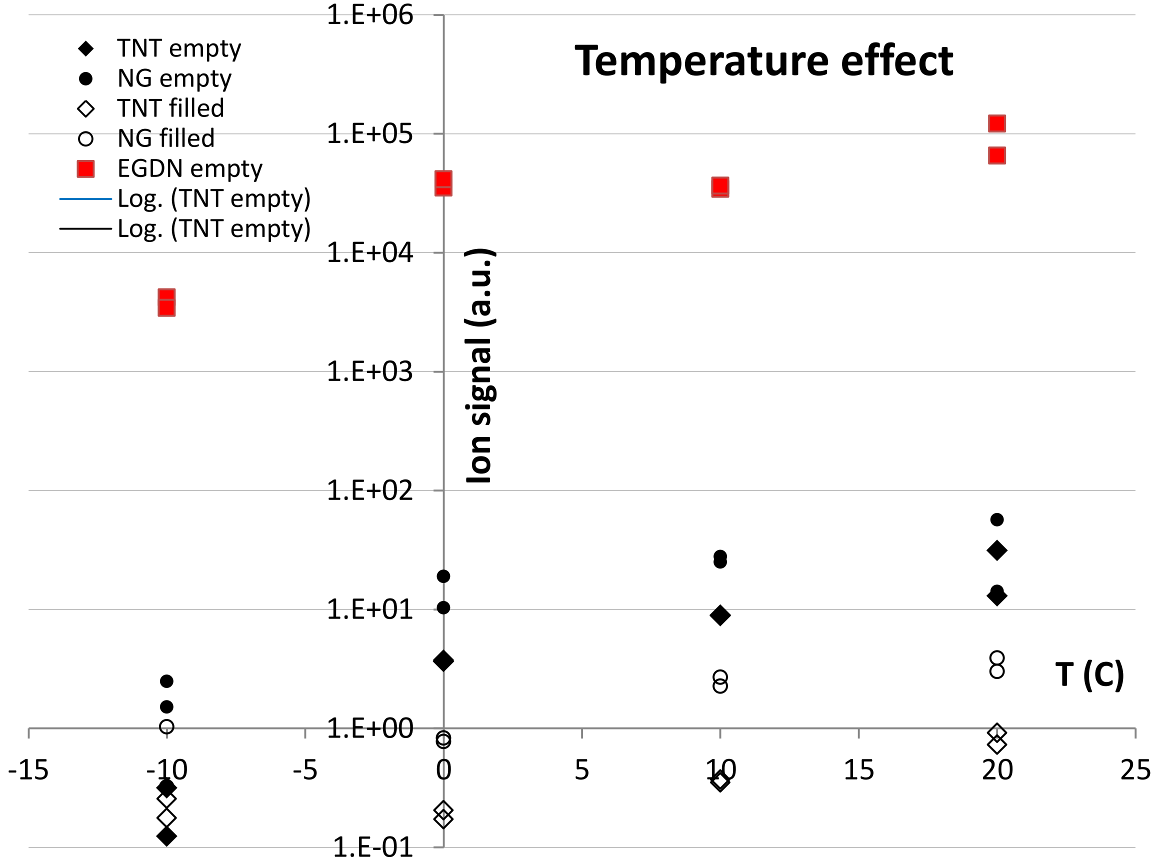
# Distance

Distance between the sampling point and the explosive in a closed truck bay modifies vapour pressure ~ TENFOLD. This rule applies to all explosives.



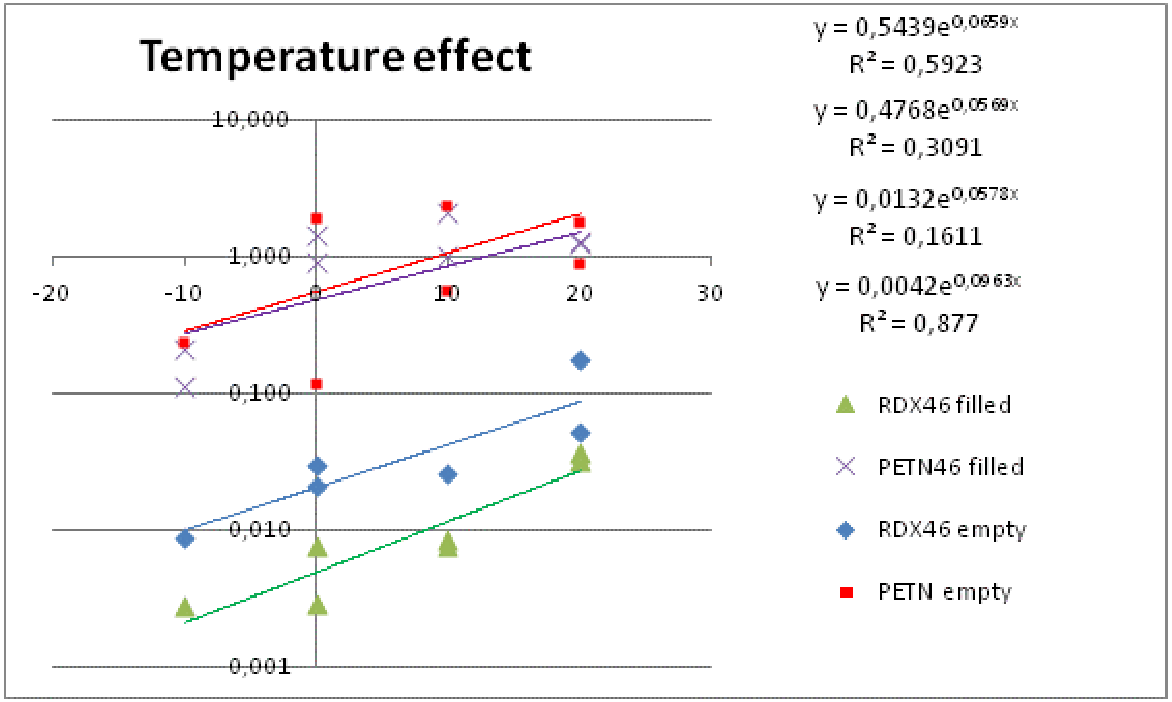

EGDN, NG, TNT, PETN and vapour pressure plotted in 3 cases: sampling point at 12 m, sampling point at 8 m, sampling point at 1m

# Temperature and cargo effect: EGDN, NG and TNT



# Temperature and cargo effect: RDX and PETN

Large refrigerated cargo container



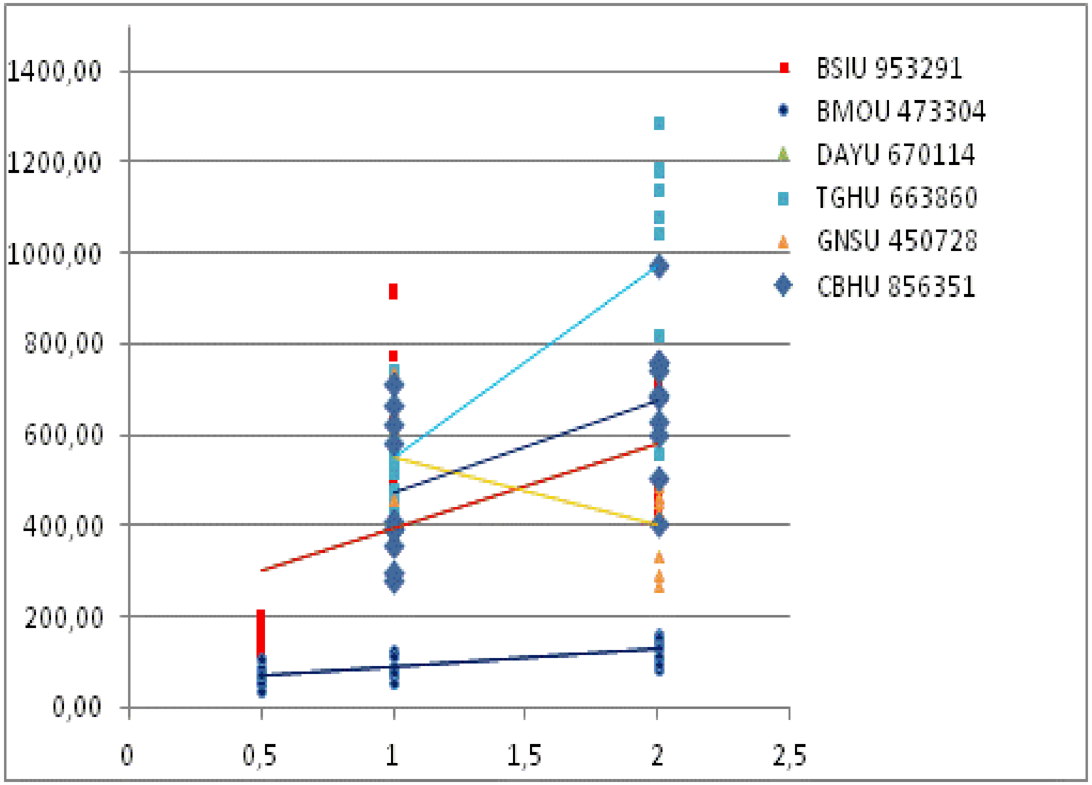

Vapor pressure increase for every 10ºC varies from a minimum factor of 1.6 to a maximum of 4.3.

Cargo reduces vapor pressure between one and two orders of magnitude

# Soaking time: EGDN

In the short run (between 30 minutes and 2 hours), soaking time effect is unpredictable. In some experiments, vapour pressure increased by a factor of 3, while in other experiments it decreased by a factor of 2. If we average, vapour pressure at 2 hours is about 50% higher than at 0.5 hours.

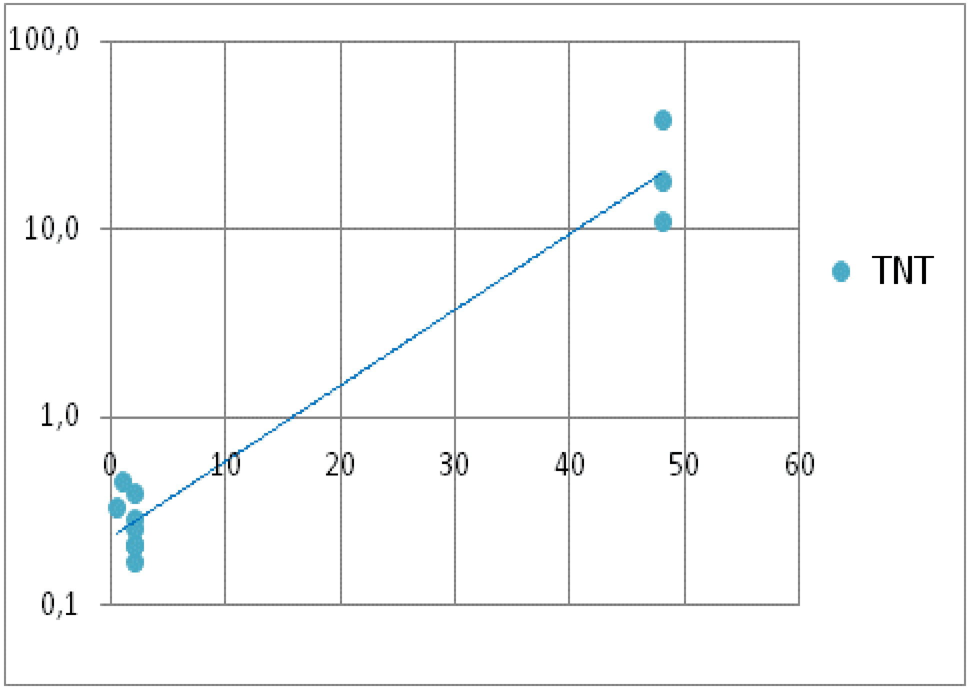
It follows at first sight that the characteristic time for the vapor to spread over the volume is tens of minutes rather than tens of hours




Soaking time (hours)

# Soaking time: TNT

In the long run, soaking time can have dramatic effects. In the Figure at right, successive samplings made at 0.5, 1 and 2 hours gave similar values. However, two days latter, vapour pressure had increased by a factor of 100. This shows that there are at least two rather different characteristic times for the vapor to spread over the volume




TNT partial pressure versus time (hours)

# Conclusions on factors affecting signal

- **The most relevant "loss factor" is the volume effect**. Vapour pressure within a truck cargo bay is typically 20,000 times lower than saturation pressure,
- **Second relevant loss factor is explosive confinement**. Although difficult to implement, since explosive handling always leaves traces, if explosive is well confined, vapour pressure drops by a factor of 1,000 (few molecules are able to cross carton/film),
- **Third relevant loss factor is the cargo itself.** Vapour pressure in a loaded truck bay is typically between 10 and 100 times lower than an empty cargo bay,
- **Fourth relevant factor is temperature**: Vapour pressure at -10ºC is typically 20 times lower than at 20ºC,
- **Fifth relevant factor is distance between the sampling point and the explosive**. Vapour pressure at 1 m from the explosive is typically 10 times lower than vapour pressure at 12m,
- **Soaking time is the less relevant loss factor**. A soaking time on the order of 2 days is needed in order for vapour pressure to increase by one order of magnitude.

# Overal picture of the vapor molecules in the cargo volume

- Small (~20 g) condensed source releases vapors according to usual diffusive release aided by thermal convection. The rapidity with which the vapor spreads through the volume is as surprising as the long term permanence of the explosive signature even under extremely cold conditions
- Large area adsorbs vapors acting as sink
- partial pressure of vapor in the gas determined as much by adsorption-desorption from these surfaces as by the release process from the source. Hence the unexpected weak dependence on temperature found
- The fact that the *sticky* explosive *stick*s to the carton and is lost is well known, but the favorable effects of the long term desorption of the vapor *stuck* had not been observed. We have found explosive contamination in containers after several months of navigation following the introduction of a small explosive sample. The surface adsorption effect is similar to that taking place in ultrahigh vacuum surface experiments, with comparable residual pressure levels.

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# Timeframe and barriers for commercialization

- The ACES instrument has been operational for over one year, with performance improving continuously
- Detector has been evaluated and continues to be evaluated at various European facilities in the UK, Holland, France, Germany and Spain
- Certification is the only pending barrier for commercialization, and is slowly proceeding in UK, Holland, France, Germany, Spain
- Estimated time frame for deployment ~ 1 year

# End

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