

Carefully to Carry

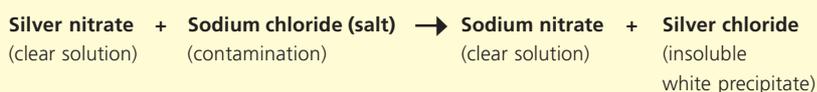
SEPTEMBER 2006

The silver nitrate test



A solution of silver nitrate in distilled water is regularly used as a simple test for the detection of seawater contamination of ships' cargoes. Whilst the test is a useful preliminary test for saline contamination it should be considered as indicative only. It has limitations and should not be relied on as definitive proof of saltwater contamination; more detailed laboratory analysis will be required to confirm this. The reaction is shown below:

This reaction results in the clear test solution turning a cloudy white as insoluble silver chloride is displaced out of the solution.



In order to undertake a 'spot' test in situ, surveyors will normally carry a small dropping/pipette bottle containing acidified silver nitrate solution. A few drops of the solution should be dropped onto both the suspected contaminated and apparently uncontaminated areas of the subject cargo.

Alternative samples of the cargo both apparently contaminated and uncontaminated should be obtained, placed into sealed plastic sample bags, and removed for later testing.

It is essential to use distilled water to wash the test samples as the presence of chloride in some waters may produce anomalous results.

The test solution should also be acidified with nitric acid to prevent the formation of other silver salts.

Laboratory identification of water origins

The source, or origin, of a particular water contamination can be identified in the laboratory by a number of different testing procedures. The testing procedures are as follows:



"The carrier shall properly and carefully load, handle, stow, carry, keep, care for and discharge the goods carried."

Hague Rules, Articles iii, Rule 2

Carefully to Carry Advisory Committee

This report was produced by the Carefully to Carry Committee – the UK P&I Club's advisory committee on cargo matters. The aim of the Carefully to Carry Committee is to reduce claims through contemporaneous advice to the Club's Members through the most efficient means available.

The committee was established in 1961 and has produced many articles on cargoes that cause claims and other cargo related issues such as hold washing, cargo securing, and ventilation.

The quality of advice given has established Carefully to Carry as a key source of guidance for shipowners and ships' officers. In addition, the articles have frequently been the source of expertise in negotiations over the settlement of claims and have also been relied on in court hearings.

In 2002 all articles were revised and published in book form as well as on disk. All articles are also available to Members on the Club website. Visit the Carefully to Carry section in the Loss Prevention area of the Club website www.ukpandi.com for more information, or contact the Loss Prevention Department.

- Quantitative chloride determination by titration.
- Quantitative determination of anions (i.e. chloride, nitrate etc) and cations (sodium, potassium etc) by ion chromatography.
- Quantitative determination of metals, such as sodium, magnesium, calcium, potassium and strontium, using either inductively coupled plasma emission spectroscopy (ICPES) or atomic absorption spectroscopy (AAS).

Test procedures

Quantitative chloride determination by titration

Two methods are available, one involving titration against standard silver nitrate solution using potassium chromate as an indicator and the other, involving titrating against a standard solution of a soluble mercury salt using diphenylcarbazone as an indicator. The chloride concentration is calculated from (i) the volume of standard silver nitrate solution used (ii) the volume of sample taken and (iii) normality/molarity (strength) of the standard solution used.

Determination of anions and cations by ion chromatography

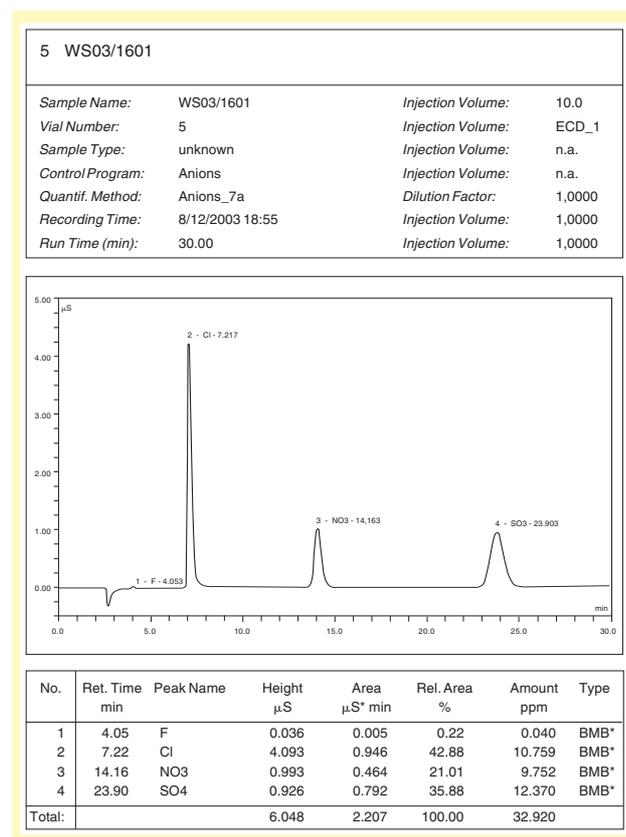
In this instrumental technique a sample (i.e. water) is introduced via an injection loop into the eluent passing through the system. The sample is then pumped through an analytical ion exchange column, which will separate the various ions (i.e. anions or cations). The separated ions are then detected using a conductivity detector and the peak areas reported are directly

related to the concentrations. The peak areas of the individual anions (i.e. chloride) are compared to standard solutions and the concentration in the actual sample calculated. Examples of a typical anion chromatogram and standard are shown below. The determination of the cations (i.e. sodium) is done separately using the same instrument but with a different eluent and column system.

Determination of cations using ICPES or AAS

These two analytical techniques will determine the concentrations of various metals/cations, such as sodium, calcium, magnesium, potassium, strontium etc in an aqueous solution. The two techniques can be described as follows:

- AAS is an analytical technique in which the sample to be analysed is converted into an atomic vapour by spraying the sample or solution of the sample into a flame. The absorbance at a selected wavelength for each individual metal/cation is measured and compared to the absorbance measurements of the sample and standard.
- ICPES is an analytical technique where the sample solution is introduced into an inductively coupled argon plasma at a temperature of approximately 8000°C. At this temperature the individual elements (cations) become thermally excited and emit light at their characteristic wavelengths. This light is collected by the spectrometer and amplified to yield an intensity measurement that can be converted to an elemental concentration by comparison with known standards.



Dry cargoes (spot test)

As noted before, for many dry cargoes such as steel, for example, an indication of seawater contamination can be achieved on site by the 'silver nitrate spot test'. The basis of the test is that addition of acidified silver nitrate to any solution containing chlorides will produce a white precipitate of insoluble silver chloride. The chloride content of most seawaters would be expected to be around the 20,000 ppm level. Therefore, the addition of acidified silver nitrate to seawater will produce a dense white precipitate making the solution appear 'milky'. The test is performed by the attending surveyor by adding a small amount of acidified silver nitrate to any contaminating water found on the dry cargo. If the resulting solution appears 'milky' then it is possible that seawater contamination has occurred. However, as stated previously, to confirm the presence of seawater further laboratory analysis will be required. An alternative to the silver nitrate spot test is to take swabs of the contaminating water, which should then be placed in a suitable airtight container and submitted to the laboratory for further analysis.

It is important to note that certain other water sources, such as brackish or river water, will contain chlorides and would also produce a 'milky' solution with the addition of acidified silver nitrate. Even domestic tap water contains enough chlorides to give a slightly 'milky' solution when tested with acidified silver nitrate.

The silver nitrate spot test should be applied to galvanised goods with caution as it gives a black precipitate due to interference from the zinc present. In addition, the silver nitrate spot test can be misleading when applied to certain types of packaging, leather goods etc, which may, themselves, contain chlorides. Control samples of uncontaminated cargo should, where possible, always be obtained and/or tested in situ.

Liquid petroleum cargoes (laboratory test)

Unlike dry cargoes, any water contamination of a liquid petroleum cargo will become either suspended within the cargo and/or percolate through and settle on the tank bottoms. The nature of the petroleum cargo will dictate whether the contaminating water will settle to the bottom of the cargo tanks. For example, a viscous fuel oil cargo is more likely to retain the water in suspension than a gasoline or kerosene cargo. Unfortunately, water contamination of a petroleum cargo will almost certainly not be spread homogeneously throughout the entire cargo, which makes representative sampling extremely difficult. However, the identification of the type of water present can be achieved using either the AAS or ICPES techniques described previously. Prior to the use of either of these techniques, the petroleum/water sample will have to be ignited and burnt until only an ash remains. This ash is then dissolved in either an acid or a flux and an aqueous solution is prepared, which is then examined using either AAS or ICPES to determine the concentrations of the metals/cations present. The analysis of samples taken from various stages of the voyage (i.e. loadport shore tanks, after loading and before discharge) can be determined. In conjunction with the actual water content, it is then possible to produce a 'cation fingerprint' of the water present in the samples taken at various stages of the voyage, which can then be used to try and identify the source of the contamination.

Water sources (fingerprinting)

There are a number of different possible sources of water, such as seawater, domestic water, distilled water, brackish water, river water, spring water, production (oilfield) water etc, and each source of water will vary depending on the geographical location. The following comments are useful in determining the type/source of any water associated with a dry or liquid cargo:

- Production (oilfield) waters have very high sodium and chloride levels, which are significantly higher than the levels found in seawater.
- The calcium levels in production waters are significantly higher than the magnesium levels, which are the reverse for seawater, where the magnesium levels are higher. The calcium/magnesium ratio is a useful indicator as to whether the water is seawater or production origin.
- River waters will vary in cation and anion levels, depending on whether it is tidal and the levels will vary during the day depending upon the state of the tide.
- Domestic tap water would be expected to have a chloride level of less than 100 ppm. However, other salts, such as magnesium, calcium etc, will vary, depending upon whether a hard or soft water area.
- The individual metal/cation concentrations will vary in seawater, depending upon the geographical location and it is possible that this type of analysis can indicate the location of the seawater. For example, the typical concentrations noted below vary significantly and the levels found say, in the Black Sea, are very much lower.
- The major cations and anions of seawater and some typical values are as shown below:

Chloride	(Cl)	18,980 mg/kg
Sodium	(Na)	10,561 mg/kg
Magnesium	(Mg)	1,272 mg/kg
Sulphate	(SO ₄)	884 mg/kg (as S) <i>but</i> 2,652 mg/kg (as SO ₄)
Calcium	(Ca)	400 mg/kg
Potassium	(K)	380 mg/kg
Bromide	(Br)	65 mg/kg
Carbonate	(CO ₃)	140 mg/kg
Strontium	(Sr)	13 mg/kg

- Brackish water is defined as water having a chloride content in excess of 2,000 ppm.

Glossary of terms

Anion: A negative ion.

Cation: A positive ion, molecule or radical.

Chromatography: A method for the separation of trace constituents of the sample by passing gaseous

mixture through a column of finely divided powder which selectively absorbs the constituents in one or more sharply divided bands.

Chromatogram: The array of distinctive bands produced by chromatography.

Eluent: The aqueous carrier of the sample through an ion chromatography system.

Ion: An electrically charged atom, radical or molecule formed by the dissolution of an electrolyte.

Molarity: Gram molecular weight, concentration of a solution.

ppm: Parts per million.

Spectroscopy: The science and practice of using spectrometers and spectroscopes in chemical analysis and studies of atoms, molecules, ions etc.