

Traceability of cleaning solutions and cleaners and disinfectants

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Tracing of cleaning solutions and hygiene products is above all a matter of food hygiene and safety. Even with fully automated systems, it is important to identify hygiene products before they are filled from road tankers into bulk storage tanks. When handling hygiene products manually, operator safety and plant safety is even more an issue. Not intended blending of products or even product solutions may cause severe accidents. In case of accidents and spillage, or simple with old stocks with damaged labels, it can be important to identify the nature of the products involved and take adequate countermeasures. Being able to identify the nature of all products used in a plant is a part of good housekeeping practices.

The intention of this paper is to show solutions for this relatively complex subject of tracing hygiene products.

Today analytical tracing and detection of most chemicals, even in very little concentrations, seems to be no longer a physical problem. When looking at product mixtures or traces of substances in a matrix chemical analysis becomes much more problematic. Considering costs of sophisticated analytical equipment, cost benefit comparisons, personnel costs and time factors many scientifically possible methods turn into theoretical options with little practical value.

However, there should be ways to control hygiene products at affordable conditions focusing on practical demands, necessities and cost benefit relations.

What are industrial cleaners?

In most cases, cleaners and sanitisers are multiple-component preparations containing sometimes up to 10 components. This leaves the question what has to be identified, detected or analysed.

An additional factor to be considered is the fact that nearly any industrial hygiene product is of technical grade. This means there must be certain allowances for variations within acceptable limits regarding the percentage of an ingredient in a formula (quality control). Furthermore, the majority of raw materials used in industrial hygiene products are of technical grade, too. By-products and variations have to be accepted within agreed specifications. This is absolutely no problem regarding the functionality of the hygiene product, but it is very well a problem regarding precise analytical data and physical parameters for product identification.

Exceptions to this rule are specially GMP manufactured products for specific industries, e.g. the pharmaceutical industry. Such products have much smaller tolerances regarding standard deviations and by-products. They are supplied with elaborate analytical background.

A possible and practical solution is the determination of summary parameters of main ingredients and the definition of acceptable deviations. In many cases, a qualitative result may be sufficient rather than a quantitative result.

For these purposes, there are various quick tests, physical instruments and analytical methods available that can be adapted to the required level of control.

These methods and their practice-oriented application are as follows:

Tracing of hygiene products may be divided into five segments:

1. Control of incoming goods, positive identification.
2. Automatic control of preparing use-solutions.
3. Control during manual handling and refilling.
4. Validations of clean surfaces free of residues from hygiene products (within legal requirements).
5. Identification in case of accidents and emergencies, e.g. unidentified spills, unlabelled containers, etc.

1. Control of incoming goods, positive identification.

Hygiene products are usually delivered to the consumer in two ways, either filled in jerry cans with sizes from usually 5, 10, 20 and 30 L, drums with 200 – 220 L, transi tanks with 800 to 1000 L, or, as bulk chemicals in road tankers.

While the containers have to be properly labelled including relevant product information, safety symbols and phrases, and batch identification. The bulk delivery has to be accompanied by a proper documentation giving the required information for identification, safe storage and handling as well as potential hazards.

An additional analytical identification of the products may serve only quality assurance reasons in case of the products in cans, drums and transi-tanks. Regarding bulk deliveries that are pumped into customer owned holding tanks still containing certain amounts left from the last delivery, it is also a safety measure to identify the product before permission for pumping is given.

Especially in the second case it will not be possible to conduct analysis that takes time and keep the transport on hold.

Which reliable, rapid methods can be used in such a case?

Measuring pH:

Scientifically correct the pH can only be measured in highly diluted solutions, because only in this case it is possible to measure the hydrogen ion concentration properly. At higher concentrations, especially in concentrated products, the measured pH becomes increasingly unreliable. Therefore, it is important to measure the pH always diluted using a consistent water quality. Preferably, demineralised water should be used.

With less sophistication, such a test can also be done with pH-paper. Testing with pH-paper may also be used in case of spills as an informative test whether a product is alkaline, neutral or acidic.

Measuring the conductivity

What is true for pH measuring applies also for conductivity measuring: only in diluted solutions scientifically correct values can be obtained. Providing a careful adaptation this method might be used for the identification of concentrates in combination with a second method.

Combining pH and conductivity

Two different products can easily have the same conductivity but still a very different composition. Finding two concentrates in one place with the same pH and conductivity is more unlikely. Therefore, a combination of both methods will dramatically improve the reliability as identification method.

Refraction indices

This is a very fast and simple method with a highly discriminating character; therefore, it is even more important to define not a standard value but a range.

When used as a third parameter along with pH and conductivity the identification is nearly 100% safe.

These methods are available as automated on-line systems as well as “hand-held” manual procedures. The required time, even for all three methods together, is less than 10 minutes, including evaluation. Alone or in any combination they can be used to safeguard bulk tank receptions or as simple quality check.

Tracers

Some products contain tracers that can be detected with a dedicated method. This is of course an indirect method that can only be used for the identification of a product type, but not as a quality control measure.

Checking other product qualities

It is even possible to identify some other compounds of cleaners with simple test, e.g. using test stripes similar to pH-paper. Available chlorine and peroxides as well as QAC can be identified with such tests, when pre-diluted under controlled conditions even approximately quantitatively.

However, a quality control of incoming goods might be interested in proper concentrations of main ingredients in hygiene products. Common and relatively easy to determine are:

Total alkalinity, total acidity, available chlorine, total peroxides, hydrogen peroxide and peroxy-acetic acid, anionic surfactants, and cationic surfactants.

With relatively inexpensive photometric equipment, there are quick tests for phosphates, and nonionic surfactants.

These easy methods permit a sufficient identification and quality control of incoming hygiene products.

According to a previous statement about the technical grade of the discussed products, it is always essential to set and agree upon ranges rather than discrete values! The tested sample has to be within the range of agreed specifications!

2. Automatic control of preparing use-solutions

In automatic cleaning systems, it is very unlikely that products are mistaken, especially when the concentrates are taken from bulk storage tanks. Here the human factor is still the highest risk when connecting jerry cans, drums or transi-tanks to cleaning systems. Transponder systems, bar code readers etc. are in discussion but cannot guarantee total safety.

The proper dilution rate and maintenance of a certain concentration in the cleaning system can often be monitored by using online conductivity meters.

In addition, there are few direct online methods to measure certain ingredients in use solutions.

Manual or semi-automatic control of use-solutions

Here we are back to summary titration of main ingredients or direct titration or analysis of main components by titration, photometric determination or even using tracers.

Control during manual handling and refilling

A very clear statement just at the beginning of this chapter:

Any manual handling of cleaning chemicals bears several high potential risks!

There is direct risk regarding the person handling chemicals. Industrial cleaners have the purpose to attack and dissolve fat and proteins – and these are main components of human body tissue!

There are risks of filling cleaners into containers with a wrong or missing labelling. The problems that could arise from these mistakes can range from insufficient cleaning via equipment damage and food contamination to full-size chemical accidents! Food contamination may occur when filling chemicals into food or food additive containers or when filling tainting materials like fuel into detergent containers!

A good example is the case of a dairy worker who filled an empty 1000 L transi-tank with nitric acid from a bulk tank. He brought the transi-tank safely with a fork lift truck to the place where it was needed and left, because his shift was finished.

About 15 minutes later the top lid of the transi-tank was blown off and a dark brown smoke column was erupting 20 meters up into the air like from a miniature vulcano. In very little time, the environment was contaminated with highly toxic nitrous gases travelling with the wind towards a near-by shopping centre. Only the immediate action of joint security forces including several fire brigade teams, paramedics, helicopters and police forces could prevent a disaster.

What happened? The worker had selected an empty container that had a proper labelling for an acid cleaner. What he did not know is that this cleaner contained organic material that must not be blended with concentrated nitric acid. The residues of about 1000 mL in the empty tank had been sufficient to start a time retarded but accelerating reaction leading to a complete decomposition of the nitric acid into nitrous gases and steam.

Because of this experience, the dairy management stopped any refilling of chemicals into other containers.

Of course, the world is not ideal and there are things we have to do and accept a compromise. To make refilling of chemicals from larger containers or bulk tanks into smaller containers as safe as possible there are professional refilling stations available. Such stations can be designed to fill

from drums into jerry cans, to fill from transi-tanks into jerry cans or to fill from bulk tanks into smaller containers.

There are also so-called user pack solutions to avoid misuse of chemical container for transporting and storing other goods. The user's packs have a closed tab that can not be removed without destroying the container. This tab fits only to a valve on the filling station.

Including personnel protection gear and hazard information, ergonomic designs for easy handling and a safety retaining area to retain spills, these refilling stations provide much more security but still cannot completely eliminate the factor of human error and failure.

4. Validations of clean surfaces free of residues from hygiene products (within legal requirements).

A complete control of a confined surface (inside of machinery, tanks and pipework) is not possible, but there are well-accepted approximation methods.

First, equipment should be designed to permit proper draining and there should be always sufficient time for draining. Research into the behaviour of common cleaning solutions has shown that after proper draining 20 – 40 mL/m² of the solution are left on equipment walls. This equals approximately 0.2 – 0.4 mL of a product when used as a 1% solution.

Secondly, these remaining solutions should be rinsed off with potable water.

This part is relatively easy to control. Mostly the cleaning solution has a conductivity or pH different from the rinse water. Then rinsing should be continued until the pH or conductivity of the incoming fresh water is no longer different from the rinse water coming out of the equipment that is rinsed.

In case of particular ingredients one can collect rinse water samples during an extended rinse cycle and analyse the samples for critical ingredients.

This more complex method is used during validation of cleaning methods in the pharmaceutical industry.

However, even this method can only show and prove a sufficient rinse time. There is still no information about what might be on the surface in the equipment!

It is a physical law that any substance having had contact with a surface leaves at least very thin molecular layers adhering to the surface. It's a question of physics (affinity surface material and kind of substance) that how much of a residue has to be expected.

Here only swab tests with suitable solvents or a placebo production with later analysis of traces will give further information.

In a normal food production, this would be impractical and not economical. A simple risk assessment would answer many questions.

Ingredients of cleaners and disinfectant for the food industry do not have a high toxicity level. Their risk potential derives mainly from their acidity or alkalinity as a concentrate and in use solution. Even this risk decreases exponentially with further dilution.

If there are any other substances that might be undesirable, as e.g. nitrates, surfactants and defoamers their application should be limited to the absolute required level.

Cleaning is normally not a single step process; alkaline cleaning is often followed by an acidic cleaning step and/or disinfection. Here the influence of the following step has to be considered and often this step can even provide a safeguarding.

A good example for this is the elimination of proteolytic enzymes by using an oxidising disinfectant. Responsible manufacturers of enzymatic cleaners use only proteolytic enzymes that can be easily destroyed by oxidation. This provides additional security in case of rinse failures. Lipolytic enzymes actually on the market are much more stable and there is no simple safeguarding method.

In case nonionic surfactants are regarded as a problem a surfactant free acidic disinfectant after the use of a surfactant containing cleaning will even further reduce the minimal residue potential.

Plant design (hygienic design) with regard to smooth surfaces providing sufficient rinse water contacts is essential. Further, there should be no dead legs and sagging sections. In combination

with a choice of adequate cleaners and sanitisers used in a proper hygiene, sequence will virtually eliminate the last risk of a food contamination by properly applied cleaners.

5. Identification in case of accidents and emergencies, e.g. unidentified spills, unlabelled containers, etc.

This last point can be mainly handled like the first point, when dealing with containers having lost their labelling. All methods described may be used to identify the product for proper elimination.

In most cases, as with spills, it is sufficient to find some basic information as:

Is it alkaline or acidic?

Does it contain available chlorine?

Does it contain peroxides?

Does it react with organic material (as concentrated sulphuric acid or peroxides)?

To answer these questions it is sufficient for most cases to use pH-paper, iodine-starch paper, peroxide test stripes, etc.

Potential hazards regarding contacts with organic material can be checked when bringing into contact with a cotton swap. A brown discoloration of the cotton or any visible reaction is an indication to treat a spill not with organic adsorbents.

Conclusion:

Tracing chemical agents and good housekeeping of chemical products is important in the light of food safety and personnel safety, and can be attained by:

Installing and maintaining good manufacturing practices

Training of operators and safety officers

Safety by design and not coincidence

Not only before receiving, handling and using chemicals they should be positively identified but also when discharging, dealing with old stocks or spills.