Carbon Dioxide Quality Incident Protection

Safeguarding against the threat of contaminated gas in soft drink bottling

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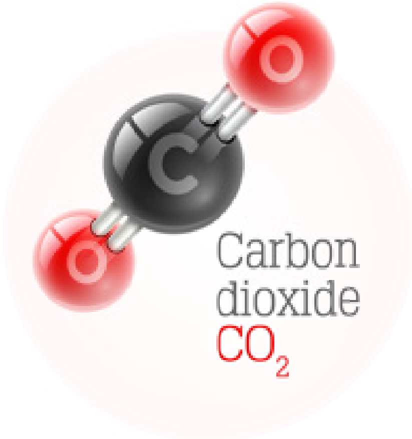
Carbonated soft drinks continue to be enormously popular beverages, consisting primarily of carbonated water, sugar, sweeteners and flavourings. Enjoyed worldwide by nearly 200 nations, at the time of writing, there are over 500 types of soft drinks on the market with an annual consumption of more than 34 billion gallons.

Danny Silk

Danny Silk is senior product manager for filtration in Parker Gas Separation and Filtration Division, United Kingdom. With over twenty years' experience, Danny is focused towards providing support and advice to the global bottling community with regards to safeguarding production processes.



The carbonation of the beverage is undertaken by forcing carbon dioxide (CO_2) into liquid and storing under pressure. The presence of this gas creates bubbles and fizzing in the liquid when pressure is reduced. The gas provides the unique taste and giving a sparkling feeling and a reduction in tasted sweetness.

The CO_2 that is injected into the beverage must be free of particles, micro-organisms and unwanted chemical compounds. Existence of these contaminants may result in a quality incident. Such an incident may occur where a delivery of out-of-specification CO_2 has been made to the plant or where CO_2 has been contaminated onsite during the production process. The effects of a quality incident are damaging, often resulting in a challenge to consumer safety, harming brand names, company reputations and revenues.

This paper discusses the issues of protecting the quality of carbon dioxide used in carbonated soft drink (CSD) applications and similar processes where security of CO_2 is of paramount importance.

Beverage standards and compliance

Hygiene legislation and quality standards are important factors for global food & beverage manufacturers as they are designed to protect both consumers and manufacturers alike. Hygiene legislation is enforceable in law and by adopting quality standards and by means of regular quality audits, a manufacture can show compliance.

Within the scope of hygiene legislation, the guidance towards preventing hazards from entering the manufacturing process and products which starts with product ingredients and on-site utilities. GMP's (Good Manufacturing Practices) ensure compliance with hygiene legislation is maintained through the successful execution of the relevant quality standard. Hygiene legislation typically requires a facility to introduce a written Food Safety Management System (FSMS) based upon the principles of HACCP (Hazard Analysis Critical Control Point).

Soft drink manufacturers face a complex range of operational demands, from the need to comply with exacting quality standards to the ability to measure new and different components as well as meeting rigorous production schedules. These are maintained with a Quality Management System

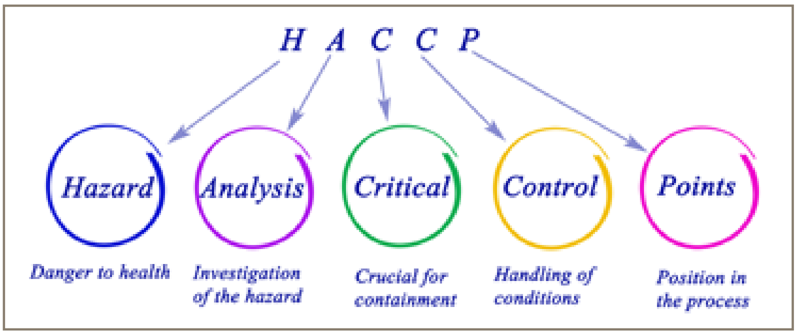
(QMS). A quality standard system has a central focus on finding and preventing nonconformities during production and supply processes thus preventing their recurring appearance.

To ensure the quality of the beverage during production, components & ingredients of products are checked, and all critical process stages for contamination of unwanted impurities. Quality assurance and quality control of ingredients is paramount to a successful product and quality compliance.

All ingredients used in soft drinks must be of high purity and food grade to obtain a quality beverage. These include the water, carbon dioxide, sugar, acids, juices, and flavours.

Here we are to focus on the carbon dioxide ingredient. As previously highlighted, carbon dioxide is used to put the fizziness in soft drinks. It is a non-toxic, inert, virtually tasteless gas. Carbon dioxide gas is injected into the product at the final stage of production. The amount of carbon dioxide added is dependent upon the type of soft drink. It is here that during the bottling or canning stage, poor quality gas can have such a damaging effect on the final product. If the gas is contaminated, then the negative effects of a quality incident may be experienced.

For Carbonated Soft Drinks (CSD), an identified HACCP CCP (critical control point) is the injection of CO_2 gas into the product. Global brand leaders have recognised the potential of consumer risk and to minimise this risk, a Standard Operating Procedure (SOP) is the inclusion of a quality incident protection device within the bottling process.



Typically global hygiene legislation & recognised food safety schemes require manufacturers to instigate written food safety management systems (FSMS). These are almost always based upon the principles of HACCP

HACCP stands for: **Hazard Analysis Critical Control Point**

CO_2 quality guidelines

Carbon dioxide (CO_2) is commercially obtained as a by-product from several sources. These include the manufacture of various chemicals, thermal decomposition of carbonaceous materials and fermentation processes. Typically, sparkling beverage sites purchase their CO_2 from an external supplier. When purchased, the CO_2 is supplied with a Certificate of Analysis (CoA). The CoA is an official signed document that certifies the analytical results from the batch of gas received. The data provided within the certificate offers reassurance that the gas meets current guideline recommendations for beverage grade gases.

The risk of contamination is not completely removed with the procurement of certified gas. Prior to delivery, certified CO_2 is at risk of contamination from atmospheric air, transportation, storage and handling, which can take place multiple times before reaching its point of use in the production plant.

There are several globally recognised bodies that provide best practice guidelines for evaluating sources of bulk liquid carbon dioxide that is to be used in the beverage product. The International Society of Beverage Technologists (ISBT) is the only international society dedicated to the scientific and technical aspects of the non-alcoholic beverage industry. The ISBT are internationally recognized as the leading supplier of technical guidelines and best practices for the beverage industry.

Published in November 2019, the 'Bulk Carbon Dioxide: Quality & Food Safety Guidelines and Analytical Methods and Techniques Reference' is recognized as the industry standard guideline. The document provides the recommended practices for commercial processing, safe handling, transport, storage, sampling, sample shipping and analytical testing of carbon dioxide as used in the beverage industry.

Beverage grade CO_2 gas has a 99.9% purity limit. The guideline provides the impurities types and their limits to produce beverage grade quality. The critical limits of the guideline are found in a supplier Certificate of Analysis, validating the delivery of beverage grade quality CO_2.

Parameter	Guideline Limit	Rationale
Purity:	99.9 % v/v min.	Process
Moisture (H_2O):	20 ppm v/v max.	Process
Oxygen (O_2):	30 ppm v/v max.	Sensory
Carbon Monoxide (CO):	10 ppm v/v max.	Process + Regulatory
Nitrogen Monoxide (NO):	2.5 ppm v/v max.	Regulatory
Nitrogen Dioxide (NO_2):	2.5 ppm v/v max.	Regulatory
Non-volatile Residue (NVR):	10 ppm w/w max.	Sensory
Non-volatile Organic Residue (NVOR):	5 ppm w/w max.	Sensory
methanol (methanol):	10 ppm v/v max.	Process
Total Volatile Hydrocarbons (THC): (as Methane)	50 ppm v/v max. (including 20 ppm v/v max. as total non-methane hydrocarbons [TNMHC])	Sensory
Acetaldehyde (AA):	0.2 ppm v/v max.	Sensory
Aromatic Hydrocarbon (AHC):	20 ppb v/v max.	Regulatory
Total Sulfur Content (TSC as S): (Total sulfur-containing impurities excluding sulfur dioxide)	0.1 ppm v/v max.	Sensory
Sulfur Dioxide (SO_2):	1 ppm v/v max.	Sensory
Odor of Solid CO_2 (Snow):	No foreign odor	Sensory
Appearance of Solid CO_2 (Snow):	No foreign appearance	Sensory
Odor & Taste in Water:	No foreign odor or taste	Sensory
Appearance in Water:	No color or turbidity	Sensory

Figure 1: Bulk Carbon Dioxide: Quality & Food Safety Guidelines and Analytical Methods and Techniques Reference 2019.

For each listed parameter, a rationale for its inclusion has been provided. Three rationale definitions are identified:

- **Sensory: Any attribute that negatively impacts the taste, appearance or odour of beverage.**
- **Process: Any attribute that defines a key parameter in a controlled process and an important consideration in the beverage industry.**
- **Regulatory: Any attribute whose limit is Set by governing regulatory agencies. Once purified to food grade and to the beverage quality levels described, the carbon dioxide must be handled to avoid contamination.**

Impurity risks

The identified impurity types all present potential risks to product quality. Off-flavour impurities may be found in Volatile Organic Compounds (VOC's). These VOC's include Acetaldehyde (AA) and dimethyl sulfide (DMS). Acetaldehyde presents an off flavour at high concentrations. DMS is detailed within Total Sulfur Content (TSC) of the ISBT guideline and has a slight odour of celery. Hydrogen sulfide (H_2S), also identified as a TSC provides the familiar rotten eggs smell.

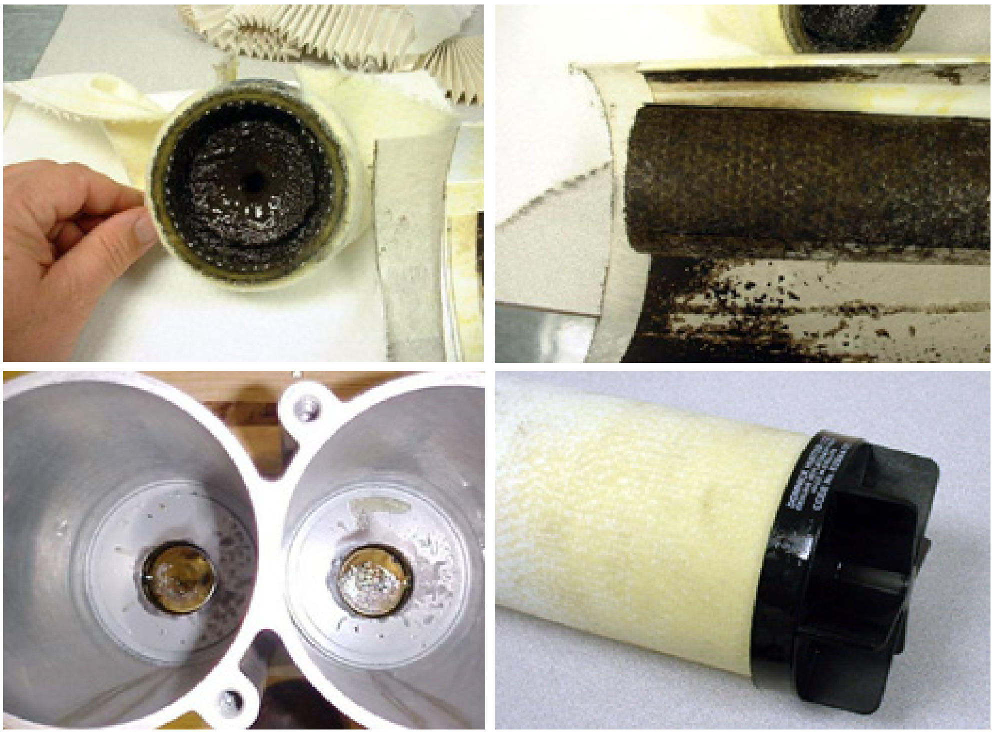
For aromatic hydrocarbon (AHC) such as benzene/toluene, a sweet, candy odor may be present. Other impurities present odor challenges and therefore it is essential to ensure that product is not spoiled, and the consumer health risk is minimised.

Outside of off-flavor impurities, other risks exist. Two common impurities include, non-volatile residue (NVR) and non-volatile organic residue (NVOR).

Non-Volatile Residue (NVR):
Consists of suspended and dissolved solid particulate matter. This may include rust, dirt and adsorbent media bed carry over such as carbon molecular sieve (CMS). Transfer wear particles such as pipe and seal deposits.

Non-Volatile Organic Residue (NVOR):
All forms of organic semi-volatiles & non-volatiles (oils, greases, plastic & elastomeric leachates) in soluble, suspended form. Examples may include hydrocarbons, ethers, organic acids and ketones.

Any contamination, even at trace levels may constitute a health risk to the consumer.



The above pictures show examples of contamination that has been successfully removed by a Parker PCO2 system.

The solution:

The dangers of unwanted impurities in beverage grade CO_2 gas is internationally recognised within the carbonated soft drinks industry with global brand leaders addressing this risk through proactive measures. One such measure is the inclusion within the manufacturing process flow of a quality incident protection device.

The Parker design formally launched through the domnick hunter brand was unique to the market when introduced in 1999. At the time of launch, several global high-profile quality incidents had been recorded. Outside of the obvious costs, both financial and reputational, there was a market requirement to address these concerns. Industry guidelines were in place and critical limits established but a proactive counter measure to neutralise threats was required.

The Parker PCO2 system is a Quality Incident Protection device which is installed to protect against poor quality contaminated gas which may pass through the supply chain and into the beverage. Originally developed over 20 years ago the PCO2 is a static adsorption bed constructed from specially selected adsorbents to remove trace contamination from CO_2. It is designed as a quality incident protection device; it will treat 'out of specification' CO_2 to return it back to within the limits of the specification.

Sometimes referenced as a 'Polisher', there is a misconception with regards to the terminology of this device. The description 'Polishing Filter' is ambiguous, the PCO2 is not designed to constantly purify poor quality CO_2. A 'polishing' approach may suggest that the beverage producer may be able to lower the incoming CO_2 specification, and then 'polish' it for safe usage. This approach must not be considered; beverage-grade quality CO_2 must be used within the bottling / canning process.

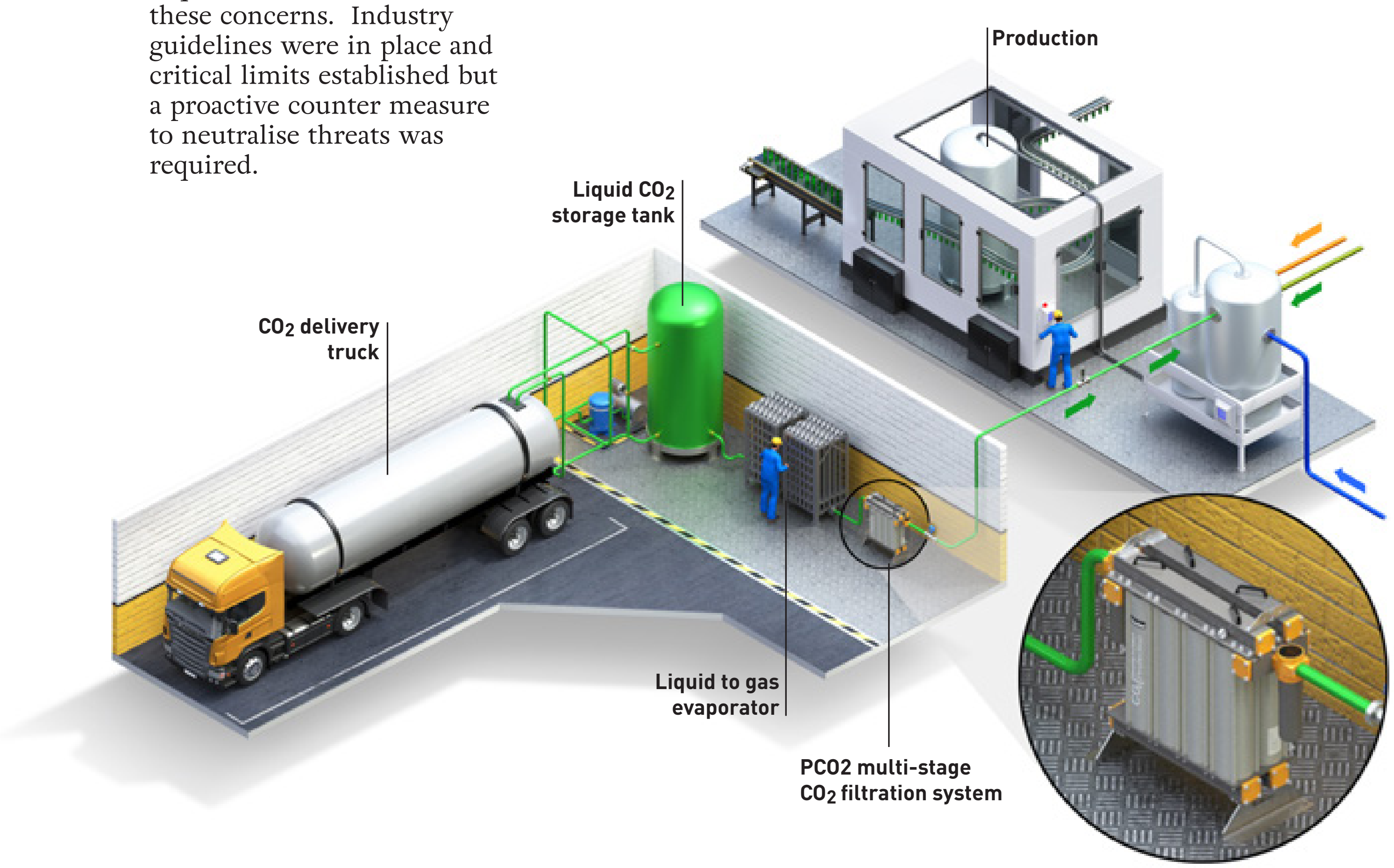


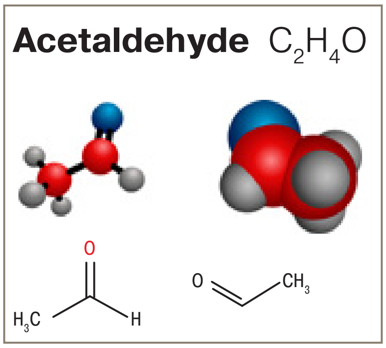
Figure 2: Typically located post CO_2 liquid evaporator the PCO2 acts as the last line of security protection from the dangers of trace contamination within the process line.

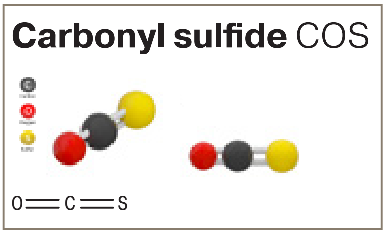
Parker unique multi-bed media technology.

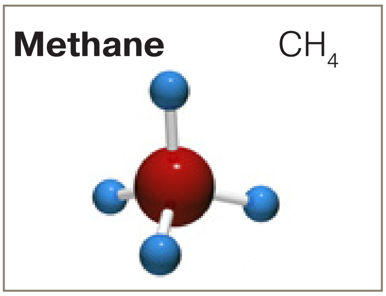
It has been established in this paper that there are many steps in place as to ensure that consumer risk is minimised from the dangers of contaminant in CO_2. These steps include the use of beverage grade gas, various quality assurance and quality control processes. It is globally recognized that despite ordering beverage-grade carbon dioxide and analysing the gas delivered, not forgetting in-line monitoring prior to use, the technology employed today offers no guarantee that trace contamination can be prevented from entering the bottle filling process.

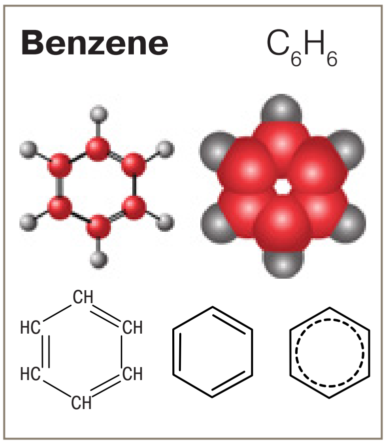
The Parker PCO2 range of carbon dioxide purifiers will remove harmful contaminants from CO_2 supplies used in the manufacture of carbonated drinks and other similar applications. These are namely: Water, ethylene glycol, hydrocarbons, olefinic hydrocarbons, ammonia, benzene, volatile oxygenated hydrocarbons, volatile sulphur compounds, carbonyl sulphide, sulphur dioxide, hydrogen sulphide and other trace impurities.

The Parker PCO2 cartridge incorporates a mix of adsorbents that effectively remove the above contamination. The addition of a particulate retention filter, providing protection down to 0.01 micron, completes a package that will ensure CO_2 conforms to the current quality guidelines for carbon dioxide. The ISBT 2019 guideline, 'Bulk Carbon Dioxide: Quality & Food Safety Guidelines and Analytical Methods and Techniques Reference' provides the critical limit points of named contaminants.









Potential Contaminant	Critical Limit ppm (v/v)	Rationale
Total Volatile Hydrocarbons (as Methane)	**50 ppm (v/v) max** of wich a minimum of 20 ppm (v/v) as total non-methane hydrocarbons.	Sensory
Total Aromatic Hydrocarbon	0.02 ppm (v/v) max.	Regulatory
Acetaldehyde	0.02 ppm (v/v) max.	Sensory
Total Sulphur (excluding SO_2, as S)	0.1 ppm (v/v) max.	Sensory

Figure 3: Shows the four main groups of potential contaminants that are generally considered to be of importance in the protection of beverage quality. All critical limits are given in v/v (volume / volume) concentrations.

Parker technology in action – the inside story

The vaporised (gas phase) carbon dioxide enters the PC02 through a 0.01-micron particulate pre-filter and into the lower manifold, which is detailed as Stage 1. At this point the pressure of the gas is indicated on the inlet pressure gauge. The lower manifold is manufactured from alocrom protected, dry powder epoxy coated aluminum extrusion and is designed to split the path of the carbon dioxide equally through the 3-layer adsorption cartridges.

The cartridges are housed within another piece of aluminum extrusion which, has also been treated in the same way as the lower manifold.

Manufactured from extruded FDA compliant aluminum, the cartridges are designed to be a perfect fit within the housing with no opportunity for bypass. The cartridges contain three different types of adsorption materials, each capable of removing different trace impurities.

The 3-layer bed consists of;

Stage 2 : Blended Dryfil® desiccant selected to effectively remove trace moisture and hydrocarbon impurities.

Stage 3 : Activated Carbon selected for the primary removal of trace hydrocarbons.

Stage 4 : Specially selected Dryfil® desiccant used for its sulphur compound removal properties.

The carefully managed adsorption bed means that the carbon dioxide passes through all three adsorbent materials, providing the opportunity for each adsorbent to perform its desired task.

The 3-layered bed is also snowstorm filled, which is a technique ensuring that the maximum amount of material can be contained within the space envelope, removing the chance of "channeling". Channeling is common in loose filled activated carbon towers. Under pressure gas will always take the path of least resistance. Over time an open channel will be created providing the carbon dioxide with a way around the activated carbon without passing through, but over it.

The main housing is completed with an aluminum upper manifold, again protected and coated. This manifold allows the carbon dioxide to form a single line and enter the 0.01-micron particle after-filter. The stage 5 filter ensures that there is no carry over into the process stream of adsorbent media.

In certain conditions, micro-organisms can be present in the CO_2 piping and storage vessels which can lead to contamination of the product. Sterile filtration may be required in these applications to prevent the introduction of microbial contaminants, such as moulds and bacteria, via the CO_2. These conditions may occur where the source of the CO_2 is derived from a fermentation process or if the source of CO_2 is unknown. In these conditions Parker supply a solution with an optional sterile grade 6th stage.

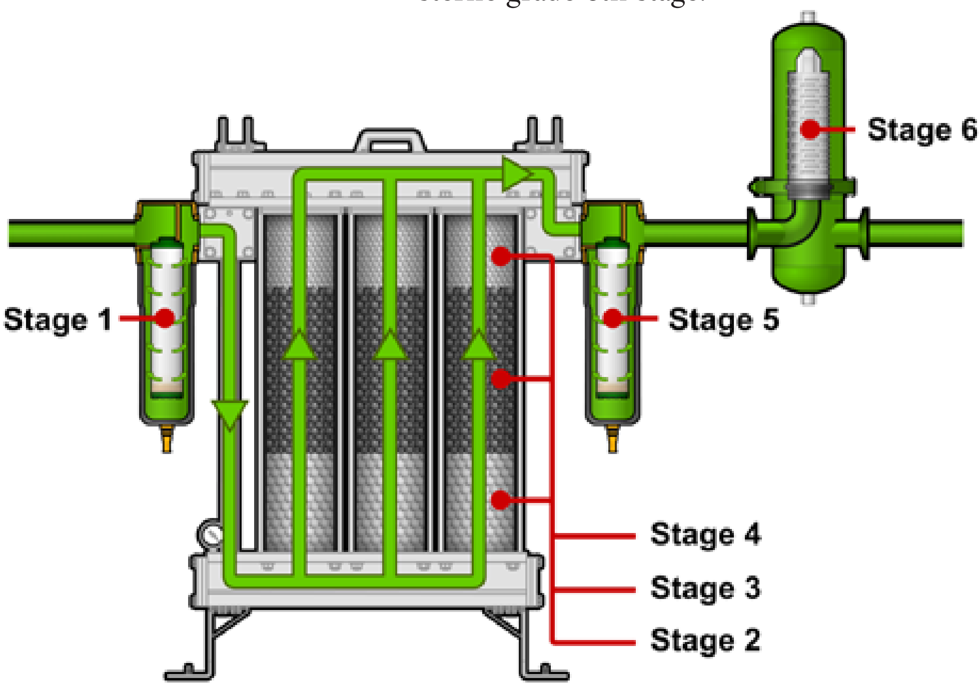


Figure 4: The three-layered adsorbent bed adsorbs contamination as it flows through. The three materials preferentially adsorb differing contaminants thus providing effective protection against a wide spectrum of potential contaminants known to create beverage flavour defects and consumer risks.

Parker multi adsorbent system advantage

Historically, the majority of beverage bottling plants reputation has been placed in the performance of an in-line activated carbon filter vessel. This vessel (or tower) has been a permanent fixture within the production process and quality assurance procedures of many bottling plants for at least the last 25 years. The efficiency of this method of protection is questionable with regards to the total protection against a quality incident. In recent times there has been a shift towards the more reliable and efficient multi-bed media approach.

A multi adsorbent system has increased retention ability over an activated carbon bed. A carbon bed will preferentially adsorb heavier hydrocarbons over more weakly attracted adsorbents. The Parker multi layered approach means that several types of molecules can be adsorbed simultaneously on the surfaces, with less competition for active sites than found in only activated carbon bed constructions. Although highly polar molecules will displace less polar molecules from the molecular sieve layer, causing the less polar ones to emerge first. As CO_2 is the least polar of the molecules in this application the 'contaminates' (VOCs, Water etc) are much more strongly attracted and hence retained within the media bed, so clean CO_2 passes through, but this process is not infinite.

Therefore, the 1st stage sorbent is extremely effective at removing the acetaldehyde and partially adsorbs some hydrocarbons. The 2nd stage removes the remaining hydrocarbons and begins removal of the sulphurs while the 3rd stage completes the removal of the sulphur compounds. The 3rd stage is vital to ensure no sulphur compounds are left in the gas stream.

Figure 5 Stages 1 to 5 detailed

Parker Media performance:

Parker multi-bed media has been tested by a 3rd party UKAS accredited laboratory to remove potential named contaminant by a factor of 10. Further details are available upon request.

We provide a detailed example, Benzene C_6H_6:

Benzene has an ISBT limit of 0.02 ppm (v), therefore the 10 times ISBT Challenge =0.2ppm (v). Third party tests confirmed the Parker media was found to adsorb the compound to a level of 0.001 and better, therefore exceeding the 10 times ISBT challenge.

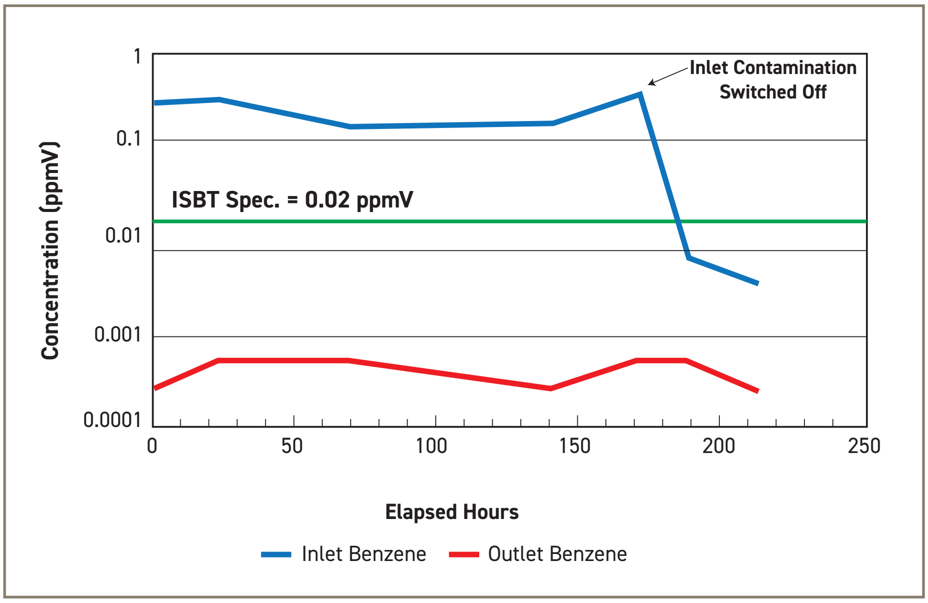


Figure 6 The inlet challenge was chosen to be at least 10 times the ISBT limit of 0.02 ppmV. The outlet concentration is below 1/10th of the ISBT limit for the duration of the test. Therefore, the filter achieves better than 100 times reduction. The contamination was removed for the final day of testing and the filter does not desorb previously adsorbed contamination.

Parker multi-bed media technology is guaranteed to treat CO_2 up to 10 times the ISBT levels of the named contaminants for a specified quantity of processed CO_2 gas. The Parker performance guarantee is based around the following assumptions:

- **The unit operates at design rated mass flow**
- **The trace contaminate levels during this time are as per ISBT guidelines (beverage grade)**
- **The system is suitably sized to meet the gas process flow requirements**

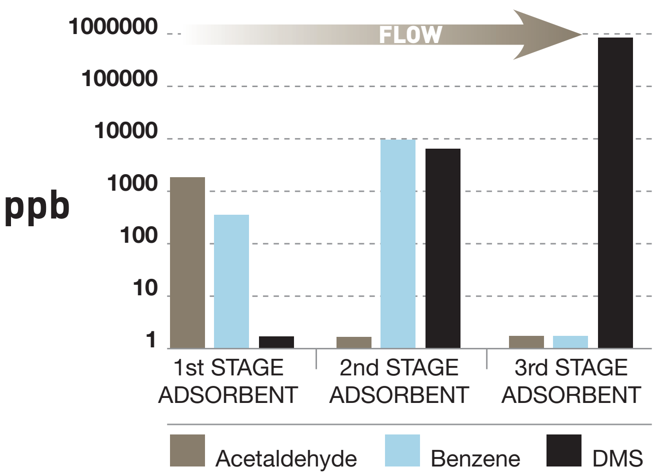


Figure 7: The graphic above shows the results of desorption analysis performed on the adsorption material removed from a used filter. By heating the sorbents, it can be determined which contaminants were removed by which part of the filter bed.
It can be seen clearly that the 1st stage adsorbent removes all the acetaldehyde, and none is left to penetrate further into the bed. The 1st stage also begins removal of the benzene but cannot remove the DMS.
The 2nd stage sorbent removes the remaining benzene and begins to remove the DMS.

The 3rd stage sorbent removes the remaining DMS.

Table 2: The benefits of 3 Layer Adsorption

Operational life- Media exchange

The adsorbent layers have a finite capacity for contaminates identified within the ISBT guidelines. There are many variables to review when trying to calculate the actual adsorbent qualities of the multi-bed media technology. Different chemical molecules are adsorbed by a differing rate by the individual media types. These are all affected by pressure flow and temperature.

A molecular sieve is a highly porous crystalline material with precise mono-dispersed pores into which certain sizes of molecules can fit, and thus, it can be used to separate one type of molecule from others. An example would be that a molecular sieve can absorb approximately 22% of moisture, The activated alumina can adsorb approximately 32% of moisture at the same condition.

The systems adsorbent beds should not be subjected to a flow over the known operational bed life for adsorbing contaminants. For PCO2 Mark 1 units supplied before July 2019, a maintenance exchange is recommended every 6 months, or after a ‘quality incident’, whichever comes first. For Next Generation units supplied after July 2019, the maintenance exchange period is extended to 12 months’ usage or after a ‘quality incident’, whichever comes first.

Parker R&D team continuously develop technologies to improve filtration and adsorption performance in line with the latest standards and guidelines. The unique ‘recipe’ of the multi-bed media is constantly under review as to ensure optimum performance to current guidelines. By using the ‘Snowstorm’ filling technique, Parker ensure that the unique media recipe is optimally packed to ensure maximum density and the best efficiency of the removal of potential contaminants.

Conclusion

Quality standards in the food and beverage industry are stringent and are under constant review. CO_2 usage is subject to active guidelines to ensure the quality of gas remains within safe limits for contaminants and impurities. Parker’s multi-bed technology is well established in bottling plants throughout the world, helping producers to reduce the risk of quality incidents. Guaranteeing that the beverage maintains its high-quality taste and they maintain brand reputation.

The Parker range of multi adsorbent PCO2 systems will ensure that CO_2 gas meets all active compliance requirements and exceeds these requirements by a factor of ten in named contaminants and impurities. The PCO2 system is essential for an effective ‘quality incident’ prevention strategy outlined for a range of CO_2 gas capacities.

For guidance on ensuring maximum security against CO_2 contaminant, please see our animation on YouTube!

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