

Effectively increase sample turnover and boost data confidence using triple quadrupole ICP-MS

Daniel Kutscher, Tomoko Vincent, Bhagyesh Surekar, Thermo Fisher Scientific

Toxic elements such as arsenic, cadmium, mercury, or lead should not be part of our daily diet, whereas other elements are added intentionally to foodstuffs to maintain a consistent level of important nutrients in a population. Verification that both types are tracked and controlled in all the food and beverages we consume is a key task for laboratories in the Food Safety market. Food analysis includes not only contaminants in a given product, but also extends to other aspects, such as verification of geographic origin using trace elemental or isotopic fingerprints or investigation of the effect of contact of the product with packaging materials under different conditions.



If lower limits of detection are required, ICP-MS is the preferred analytical solution. Modern instruments offer comprehensive interference removal and innovative solutions to increase sample throughput. Moreover, ICP-MS can be coupled to different chromatographic techniques, such as ion chromatography (IC). For some elements, speciation analysis is required to determine the chemical form in which an element is present.

Single quadrupole ICP-MS systems are commonly used for screening a wide range of samples for both toxic as well as nutritional elements, combining consistent interference removal with short measurement times. This is especially true when complemented by a secondary interference removal mechanism, such as an automated low mass cut off [1]. Interference removal is accomplished by using a collision/reaction cell (CRC) flushed with helium to remove the most common polyatomic interferences. In some cases, reactive gases, such as hydrogen, oxygen, or ammonia are used to eliminate certain interferences (e.g., H₂ for reduction of ⁴⁰Ar₂⁺ on ⁸⁰Se), but often, the formation of new interferences caused by these gases in the collision cell is a serious issue, as other ions present in the ion beam can lead to unwanted side reactions.

One way to overcome the challenges of interferences is to use triple quadrupole ICP-MS (TQ-ICP-MS) instrumentation [2], such as the Thermo Scientific™ iCAP™ TQe ICP-MS. TQ-ICP-MS instruments eliminate interferences through the use of reactive gases flushed into the CRC (often also referred to as quadrupole 2 (Q2), independent of its constructional shape). Interference removal is accomplished as analyte and interference react differently with the collision/reaction gas and can be separated from each other in the analysing quadrupole (Q3). The occurrence of side reactions is effectively suppressed through a mass filtration step prior to the CRC in the first quadrupole (Q1), added to the mass analyser axially in front of the CRC (Q2).

Experimental

An iCAP TQe ICP-MS system was used for all analysis [3]. On each day of measurement, performance of the instrument was verified in an automatic report and tuned using the autotune routines in case performance criteria were not met. The optimised parameters for the analysis of food samples are summarised in Table 1. Complementary measurements using hydrogen as a reactive gas were accomplished using a Thermo Scientific™ iCAP™ RQ ICP-MS.

The selection of the optimum measurement mode for each analyte can be easily achieved using the Reaction Finder Method Development Assistant included in the Thermo Scientific™ Qtegra™ ISDS Software. For single mode analysis, settings proposed by Reaction Finder were modified manually.

Table 1. Instrument configuration and operating parameters.

Parameter	Value
Nebuliser	Borosilicate glass MicroMist (Glass Expansion, Australia), 400 µL·min ⁻¹ , pumped at 40 rpm
Spraychamber	Quartz cyclonic spraychamber cooled at 3 °C
Injector	2.5 mm quartz
Interface	Ni sampler and Ni skimmer with 3.5 mm insert
Forward power	1550 W
Nebuliser gas	1.00 mL·min ⁻¹
TQ-O ₂	O ₂ gas at 0.34 mL·min ⁻¹
SQ-KED	He gas at 4.3 mL·min ⁻¹ with 3 V KED

Results and Discussion

Kinetic energy discrimination (KED) allows analysis of elements over the full mass range (lithium to uranium), enabling removal of polyatomic interferences in the most affected mass range (*m/z* 40–100) without significantly compromising detection limits (over the so-called standard (no cell gas) mode). However, there are certain elements, which, if present in sample, can lead to the formation of interferences not removable using KED. False positive results caused by the presence of interferences can present a significant disruption to the daily workplan in a busy laboratory, as they require troubleshooting and re-analysis, during which time the instrument affected will have to stop productive analysis. To illustrate the process of interference removal on a triple quadrupole ICP-MS, Figure 1 contains an overview on the analysis of ⁷⁵As and ¹¹¹Cd, demonstrating the two potential pathways of measurement: A mass shift reaction (the analyte is reactive to a specific gas), or an on-mass reaction (the interference reacts while the analyte is detected on its original *m/z* ratio).

A key interference for the often-critical analytes arsenic and selenium can arise from the presence of rare earth elements (REE), such as gadolinium (Gd), samarium (Sm), or neodymium (Nd). These elements readily form doubly charged ions (M⁺⁺) in the plasma, which cause false positive results on arsenic (from ¹⁵⁰Sm⁺⁺ and ¹⁵⁰Nd⁺⁺) and selenium (¹⁵⁴Gd⁺⁺, ¹⁵⁶Gd⁺⁺ and ¹⁶⁰Gd⁺⁺). This is because mass spectrometers detect the mass to charge ratio of a given ion rather than detecting its mass directly. To illustrate this, a comparison of results for two standard reference materials, NIST 1515 (apple leaves) and NIST 1573 (tomato leaves) is shown in Table 2. NIST 1515 contains approximately 17 mg·kg⁻¹ of neodymium and 3 mg·kg⁻¹ of gadolinium (dry weight), which translate to approximate concentrations of 85 µg·L⁻¹ and 15 µg·L⁻¹, respectively in the measured solution (assuming a 200-fold dilution through sample preparation).

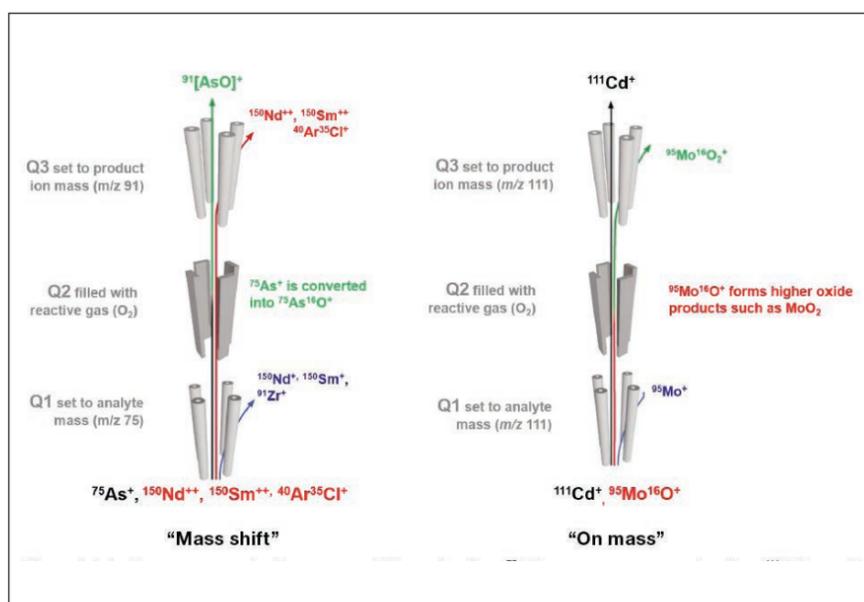


Figure 1. Interference removal using a mass shift reaction (e.g. ^{75}As) or an on-mass reaction (e.g. ^{111}Cd) on a triple quadrupole ICP-MS.

Table 2. Comparison of results for NIST SRM 1515 (apple leaves) and 1573 (tomato leaves), showing severe false positive results obtained in KED mode.

	Analysis mode	Measured [$\text{mg}\cdot\text{kg}^{-1}$]	Certified [$\text{mg}\cdot\text{kg}^{-1}$]
Arsenic (^{75}As)	KED	0.469 ± 0.012	0.038 ± 0.007
	TQ- O_2	0.036 ± 0.003	0.038 ± 0.007
Selenium (^{78}Se)	KED	1.272 ± 1.87	0.050 ± 0.009
	TQ- O_2	0.052 ± 0.006	0.050 ± 0.009

Cadmium, another critical contaminant, can be interfered by molybdenum if present in only slightly elevated concentrations (above $30\text{--}50\ \mu\text{g}\cdot\text{L}^{-1}$) in the analysed solution. This could be the case for sample types containing naturally higher amounts of molybdenum, such as cereals, legumes, or soy and soy products, even considering the dilution effect during sample preparation. Again, an elevation of the signal of the commonly analysed ^{111}Cd isotope (through $^{95}\text{Mo}^{16}\text{O}^+$ interference) would result in an undiscovered false positive result. As a single quadrupole ICP-MS would not distinguish between isobaric $^{111}\text{Cd}^+$ and $^{95}\text{Mo}^{16}\text{O}^+$, even small contributions from the interference alongside a genuine cadmium signal could lead to a false positive result. The results of the analysis of cadmium in the presence of molybdenum are summarised in Table 3. Please note that also other relevant isotopes of cadmium would be similarly affected by MoO interferences (e.g. ^{110}Cd , ^{112}Cd , and ^{114}Cd).

Table 3. Results obtained for the analysis of cadmium in the presence of varying amounts of molybdenum in different modes of analysis.

Mo concentration	^{111}Cd (SQ-KED) [$\mu\text{g}\cdot\text{L}^{-1}$]	^{111}Cd (TQ- O_2) [$\mu\text{g}\cdot\text{L}^{-1}$]
$0.1\ \text{mg}\cdot\text{L}^{-1}$	0.030	<0.001
$1\ \text{mg}\cdot\text{L}^{-1}$	0.322	<0.001
$10\ \text{mg}\cdot\text{L}^{-1}$	2.932	0.001

Another opportunity for improvement over what KED operation can achieve is the suppression of the background created by argon based polyatomic interferences on elements such as ^{56}Fe (through $^{40}\text{Ar}^{16}\text{O}^+$) and ^{80}Se (through $^{40}\text{Ar}_2^+$). To overcome these interferences, reactive gases such as hydrogen can be used in a method, providing typically lower detection limits for these elements, but extending the method runtime. Table 4 shows a comparison of the analytical figures of merit comparing calibration curves obtained in SQ-KED, SQ- H_2 and TQ- O_2 modes. As can be seen, the use of hydrogen helps to improve detection limit significantly, but with no solution to the above mentioned false positive results caused by the presence of neodymium and gadolinium. Using oxygen as a reactive gas in conjunction with a triple quadrupole mass analyser, these interferences are fully removed and identical detection limits are achieved (Table 4).

Although the use of O_2 on a single quadrupole ICP-MS would lead to equally unaffected results in the presence of rare earth elements, its main limitation is again the lack of suppression of unwanted side reactions. Other elements present in the sample (e.g., molybdenum in the case of selenium) could contribute to the signal observed on the new product ion mass (^{96}Mo vs. $^{96}[\text{Se}^{16}\text{O}]^+$). Although molybdenum is reactive to oxygen as well (forming MoO and MoO_2 readily), its contribution to $m/z\ 96$ can only be eliminated through mass filtration in Q1, and therefore a triple quadrupole mass spectrometer is required.

Table 4. Analytical performance for the analysis of selenium using different modes.

	^{78}Se (SQ-KED)	^{78}Se (SQ- H_2)	^{80}Se (TQ- O_2)
IDL [$\text{ng}\cdot\text{L}^{-1}$]	17.5	0.7	0.7
BEC [$\text{ng}\cdot\text{L}^{-1}$]	10.1	2.5	0.3
BEC in sample containing REE [$\mu\text{g}\cdot\text{L}^{-1}$]	6.3*	4.7**	0.00*

* Solution containing $10\ \mu\text{g}\cdot\text{L}^{-1}$ of all REE (Ce-Lu)

** Solution containing $1000\ \mu\text{g}\cdot\text{L}^{-1}$ of all REE (Ce-Lu) [4]

Impact on sample throughput

Another common challenge in food testing laboratories is the need to analyse a high number of samples to keep up with the backlog and achieve return on investment. TQ-ICP-MS systems are therefore less commonly found in analytical testing laboratories, as each specialised set of measurement parameters (e.g., for multiple reactive gases) adds to the total method runtime. In contrast, SQ-ICP-MS allows for the analysis of samples using one or two acquisition modes only.

However, a potential alternative to achieve both high throughput and full interference removal is the use of a single mode based on triple quadrupole technology (enabling pre-filtration of the ion beam prior to the CRC) and oxygen as a reactive cell gas. In this case, the iCAP TQe ICP-MS is operated in a single mode for all elements, with the use of O_2 as a reactive gas. This allows for effective removal of all interferences, including polyatomic species and doubly charged rare earth element ions, across the entire mass range.

A total of 40 individual isotopes were monitored (simulating an ample set of common analytes plus appropriate internal standards) using different methods typically used on single and triple quadrupole ICP-MS. In all cases, an identical sample delivery system was used (a standard autosampler) with identical uptake and rinse times (30 seconds each).

Table 5. Comparison of runtime, batch runtime, and interference removal capability for different ICP-MS methods.

	SQ-ICP-MS		TQ-ICP-MS TQ- O_2	
	KED Single Mode	KED and H_2	TQ- O_2 Single Mode	SQ-KED and TQ- O_2
Analysis time per sample including uptake/wash [s]	200	239	200	217
Total runtime [min] and time saving for 100 samples	333 + 0 min	398 + 65 min	333 + 0 min	362 + 31 min
Polyatomic interferences	Yes	Yes	Yes	Yes
Doubly charged interferences removed (e.g., REE)	No	No	Yes	Yes
Confidence all interferences are under control	No	No	Yes	Yes

As can be seen from the data in Table 5, a single mode analysis has a clear potential for the realisation of time savings, especially compared to a method combining the use of KED with H_2 . Here, the sample turnover time is not only extended because of the need to evacuate and flush the CRC with two different gases (He for KED operation, and H_2), but additionally through the longer duration of this process when adding a gas with a high flow rate (often in the range of 7 to $10\ \text{mL}\cdot\text{min}^{-1}$ for H_2) and a high diffusion coefficient. Whereas a single mode analysis using KED mode would be able to overcome the most challenging polyatomic interferences, a single mode analysis combining pre-filtration of the ion beam for each analyte and the use of O_2 as a reactive gas would enable identical sample turnover times to be achieved with the certainty that also other, often unexpected, interferences are fully eliminated.

A comparison of the detection limits for a variety of common analytes is shown in Table 6. As can be seen, for elements commonly analysed using KED, there is no significant negative impact on the achievable detection limits. In contrast, most elements can be detected at a similar concentration level, whereas several can be detected at even lower levels in the TQ- O_2 mode. The reason for the little to no impact observed is found in the applied bias potentials between the CRC and the analysing quadrupole. Whereas in KED mode, a positive bias potential of typically around $3\ \text{V}$ is used, the bias potentials in reactive gas modes are usually set to a negative difference of up to $7\ \text{V}$, allowing part of the signal loss (due to kinetic energy loss on collisions of the target ions with the cell gas) to be offset.

Table 6. Comparison of detection limits obtained in SQ-KED mode and TQ-O₂ mode (elements benefitting from superior interference removal, such as arsenic and selenium are not considered in this comparison). In the 'Comparison' row, the symbol + denotes an improvement of TQ-O₂ mode vs. KED mode in the resulting LOD, whereas O denotes equivalent performance.

Element	¹¹ B	²³ Na	²⁴ Mg	³⁹ K	⁵⁵ Mn	⁵⁹ Co
LOD [$\mu\text{g}\cdot\text{L}^{-1}$] KED mode	0.4	4	1	3	0.003	0.011
LOD [$\mu\text{g}\cdot\text{L}^{-1}$] TQ-O ₂ single mode	0.4	0.92	0.20	0.17	0.006	0.003
Comparison	O	+	+	+	O	+

Element	⁶⁰ Ni	⁶³ Cu	⁶⁶ Zn	⁸⁵ Rb	⁸⁸ Sr	⁹⁸ Mo
LOD [$\mu\text{g}\cdot\text{L}^{-1}$] KED mode	0.023	0.09	0.03	0.004	0.002	0.003
LOD [$\mu\text{g}\cdot\text{L}^{-1}$] TQ-O ₂ single mode	0.005	0.02	0.04	0.005	0.009	0.008
Comparison	+	O	O	O	O	O

Element	¹¹¹ Cd	¹²¹ Sb	¹³⁸ Ba	²⁰⁸ Pb	²³⁸ U
LOD [$\mu\text{g}\cdot\text{L}^{-1}$] KED mode	0.001	0.001	0.002	0.001	0.001
LOD [$\mu\text{g}\cdot\text{L}^{-1}$] TQ-O ₂ single mode	0.0004	0.003	0.006	0.005	0.0003
Comparison	+	O	O	O	+

Conclusion

As demonstrated in this note, the use of TQ ICP-MS with a combination of helium and oxygen as collision/reaction gases is a powerful approach to address the challenges caused by the presence of rare earth elements and their associated interferences. With this technology, existing and established methods can be transferred and extended for improved interference removal on key analytes and new options become available. In addition as shown, a reduction in analysis time of between 10% and 20% compared to methods based on either single or triple quadrupole ICP-MS using different collision/reaction gases is possible, without an impact on detection limits.

The iCAP TQe ICP-MS enables complete removal of many commonly encountered interferences, providing not only significantly reduced detection limits for key analytes, but also increasing confidence in data quality. With no additional investment in laboratory infrastructure on top of what is required for a single quadrupole instrument (only the common gases helium and oxygen are required for interference removal), unnecessary interruptions to the daily laboratory routine caused by unexpected false positive results can be avoided.

References

1. Thermo Scientific Smart Note 44415: iCAP RQ ICP-MS <https://assets.thermofisher.com/TFS-Assets/CMD/brochures/sn-44415-icp-ms-single-quadrupole-sn44415-en.pdf>
2. Thermo Scientific Smart Note 44452: iCAP TQ ICP-MS <https://assets.thermofisher.com/TFS-Assets/CMD/brochures/sn-44452-icp-ms-triple-quad-sn44452-en.pdf>
3. Thermo Scientific Application Note 44474: Maximising laboratory throughput: robust and accurate analysis of trace metals in food samples with triple quadrupole ICP-MS <https://assets.thermofisher.com/TFS-Assets/CMD/brochures/sn-44474-icp-ms-triple-quad-sn44474-en.pdf>
4. Thermo Scientific Application Note 43285: Accurate determination of arsenic and selenium in environmental samples using triple quadrupole ICP-MS <https://assets.thermofisher.com/TFS-Assets/CMD/Application-Notes/AN-43285-ICP-MS-Arsenic-Selenium-Sediment-Rock-AN43285-EN.pdf>

Learn about the determination of trace elements in a variety of food samples, including both organic as well as non-organic foods. Download the application note "Maximising laboratory throughput: Robust and accurate analysis of trace metals in food samples with triple quadrupole ICP-MS" at www.thermofisher.com/food-tracemetals-icpms

Find out more at thermofisher.com/TQ-ICP-MS



Read, Share and Comment on this Article, visit: www.labmate-online.com/article

Knife Mill Provides Fast Cryogenic Homogenisation of Food Samples

Retsch's knife mill GRINDOMIX GM 200 is employed in laboratories all over the world for the homogenisation of food samples as well as samples with a high water, oil, sugar or fat content. A range of new accessories makes it now suitable for cryogenic grinding of moist samples without addition of water or of very sticky samples, using dry ice.

The so-called cryo kit offered by Retsch consists of a full metal knife and a special stainless-steel grinding container with lid. The knife used for cryogenic grinding has four blades and is made entirely of steel. This makes it much more resistant against embrittlement and hard impact effects - which occur when frozen food is processed - than the standard knife with plastic components. For the same reason, the stainless-steel grinding container should be used for hard samples. This container is specially designed for cryogenic grinding, with baffles that ensure thorough mixing of the sample and, as a result, optimum homogenisation. To prevent overpressure inside the closed jar caused by the frozen CO₂ which is warmed during the grinding process with dry ice and evaporates, the special lid features a small opening to let carbon dioxide escape.

The GRINDOMIX GM 200 knife mill covers a wide application range, from granular products like rape seed, rice, soybeans to fibrous or tough samples like meat, fish, candy, cheese or plants. It processes sample volumes up to 700 ml quickly and effectively. Thanks to reproducible setting of parameters, programs and sequences, this mill ensures analytical results with minimum standard deviation.

More information online: ilmt.co/PL/qDEo

For More Info, email: 54564pr@reply-direct.com



Achieve Quality Assurance Within Your Food and Beverage Laboratory

Whether it's the water quality, the product itself or the production process, the new Turb[®] 750 IR turbidity meter from Xylem's WTW brand is equipped for a myriad of quality assurance tasks within the food and beverage laboratory.

Checking the turbidity of incoming water, especially from a local aquifer in order to prevent overuse, requires high performance measurement at low values. The intelligent IRPC check for best precision, reproducibility and plausibility supports this need.

The Turb[®] 750 IR cleverly uses infrared optics to avoid natural but disruptive absorption effects experienced by traditional 'white light' turbidimeters when measuring coloured concentrates or end products like juices or wine. Additionally, the many AQA options (such as the AQS key for proof standard) guarantees best data security with extensive data management from sample IDs to data filters for batch transfer to LIMS.

Using the Turb[®] 750 IR to measure the turbidity of washing water between batch runs in a production line is also proven to safeguard health as low suspended solids correlates to a risk reduction of spreading allergenic substances into the next product.

The Turb[®] 750 IR offers an excellent price/performance ratio; especially considering its simple operation, data handling and AQA functions.

More information online: ilmt.co/PL/LZa9

For More Info, email: 54426pr@reply-direct.com



Portable Conductivity Meter for Regulatory Testing of Drinking Water

Checking water quality, in applications as diverse as regulatory testing of drinking water and swimming pool maintenance, is easy with the CA10141 portable conductivity meter from Chauvin Arnoux. This compact, handheld instrument, which features a fully waterproof design with an IP67 ingress protection rating, offers fast and reliable measurement of conductivity, TDS (total dissolved solids), salinity and temperature with all results clearly displayed on a large backlit LCD screen.

Simplicity of operation and rugged construction combined with high accuracy make this novel instrument an ideal choice for use wherever it is necessary to monitor water quality. Typical applications include checking drinking water in compliance with the Drinking Water Directive 98/83/EC, checking salinity and conductivity of water used in food manufacturing processes, measuring the conductivity of water in industrial boilers, confirming water quality in swimming pools and monitoring water in natural pools and rivers as an aid to detecting pollution.

The CA10141 conductivity meter can measure conductivity over the range 0.050 µS/cm to 500.0 mS/cm, TDS from 0.001 mg/l to 499.9 g/l, and salinity from 2.0 to 42.0 psu. It also records the temperature at which the measurements are made over the range -10.0 to +120°C. In addition to showing the results on its integral LCD screen, the instrument also records them in its internal memory. This can store up to 30,000 time and date-stamped measurements which can subsequently be transferred, via a standard USB link, to a PC for analysis, reporting or archiving.

Equally suitable for use in the laboratory or on site, the Chauvin Arnoux CA10141 portable conductivity meter is supplied as standard in a rigid padded carrying case, together with an XCP4ST1 Capec four-pole conductivity cell with built-in Pt1000 temperature sensor. Also included are a ready-to-use 1408 µS/cm conductivity standard, a plastic beaker, a wrist strap and a quick-start guide. Other conductivity standards are available as options, as are adaptors for using conductivity cells with DIN, BNC, S7 and jack connectors.

For More Info, email: 54236pr@reply-direct.com



Listeria monocytogenes Diagnostic Test Earns AOAC Performance Tested Method Certification

Nemis Technologies Ltd has announced that its N-Light[™] *Listeria monocytogenes* diagnostic test designed for food safety has officially earned the prestigious AOAC[®] Performance Tested MethodSM(PTM) Certificate from the AOAC Research Institute in the US, the industry's leading product certification organisation.

The groundbreaking AquaSpark[™] platform technology behind Nemis N-Light[™] tests offers a unique and powerful alternative to existing diagnostic methods providing food producers and processors with the first reliable on-site method that conveniently enables rapid lab-free testing of work surfaces at any point in the supply chain.

Arnaud Muller, the company's CEO, stated: "We are extremely proud to receive the validation of our N-Light[™] *Listeria monocytogenes* kit from AOAC in the food safety arena. At Nemis, the team aspire to create a safe food value chain so none of the most vulnerable consumers will be exposed to unsafe products. Thanks to our game-changing innovation, thousands of food producers and processors worldwide determined to maintain high quality standards and protect their brands from damaging product recalls, will be able to improve the safety and quality of their products while driving cost savings. We will be launching very soon in Switzerland and in Europe."

Dr Mario Hupfeld, the company's CSO added: "Our goal was to develop and validate a *Listeria monocytogenes* environmental monitoring protocol that provides food customers in the least amount of time possible with the information they require to implement an effective seek and destroy approach without delay. Our revolutionary protocol identifies *Listeria monocytogenes* with matchless sensitivity and specificity, yielding results from an environmental swab overnight. This protocol from sampling collection to results reading and interpretation can be performed by anyone at any time and on-site thanks to our innovative biosafety cap."

More information online: ilmt.co/PL/dprR

For More Info, email: 54233pr@reply-direct.com