

Determination of Chlorate, Perchlorate and Bromate in Food Commodities using LC-MS/MS with Atlantis Premier BEH C18 AX Column

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INTRODUCTION

Chlorate and perchlorate are ubiquitous contaminants that have been detected in food commodities. Chlorate is formed as a disinfection byproduct of water used in food production or for cleaning surfaces in contact with food while perchlorate can be found via the use of fertilizers.¹ Chlorate and perchlorate pose a high risk to human health especially amongst infants and children by inhibiting iodine uptake while bromate has been classed as a possible human carcinogen.^{1,2} Thus, it is important to routinely monitor these compounds at trace levels in food commodities to check compliance with regulatory limits. Chlorate and perchlorate have been previously determined in infant milk using the Anionic Polar Pesticide (APP) Column.³ However, the established method involved the use of a high ammonium formate buffer concentration which can result in signal suppression. The objective of this study was to establish an efficient method for analysis of chlorate, perchlorate and bromate using the Atlantis™ Premier BEH™ C18 AX Column and ACQUITY™ Premier UPLC™ System coupled to Xevo™ TQ Absolute MS System.

METHODS

Matrix-matched standards were prepared in cucumber and infant formula using the EURL Quick Polar Pesticides (QuPPE) PO and AO methods respectively over a range of 5 – 200 µg/kg.⁴ The sensitivity of the method was evaluated by assessment of the response of matrix-matched standards prepared in infant formula at 0.1 - 20 µg/kg.

LC System	ACQUITY Premier UPLC System
MS System	Xevo TQ Absolute MS
Ionisation mode	ESI -
Acquisition mode	MRM
Column	Atlantis Premier BEH C18 AX Column, 2.1 x 100 mm, 1.7 µm
Mobile Phase A	10mM ammonium formate + 0.1% Formic acid in water
Mobile Phase B	0.1% Formic acid in acetonitrile
Software	waters_connect™ Software for Quantitation



ACQUITY PREMIER XEVO TQ ABSOLUTE

Compound	Retention time (min)	MRM transition	Cone voltage (V)	Collision energy (V)
Bromate	1.25	127 > 111	50	18
Bromate	1.25	127 > 95	50	22
Bromate- ¹⁸ O ₃	1.25	133 > 97	55	24
Chlorate	1.45	83 > 67	55	15
Chlorate	1.45	83 > 51	55	17
Chlorate- ¹⁸ O ₃	1.45	89 > 71	33	15
Perchlorate	1.97	99 > 83	65	18
Perchlorate	1.97	99 > 67	65	42
Perchlorate- ¹⁸ O ₄	1.97	107 > 89	55	20

Table 2. MRM Parameters for chlorate, perchlorate and bromate.



Atlantis PREMIER Columns

Table 1. Instrument and chromatographic conditions.

RESULTS

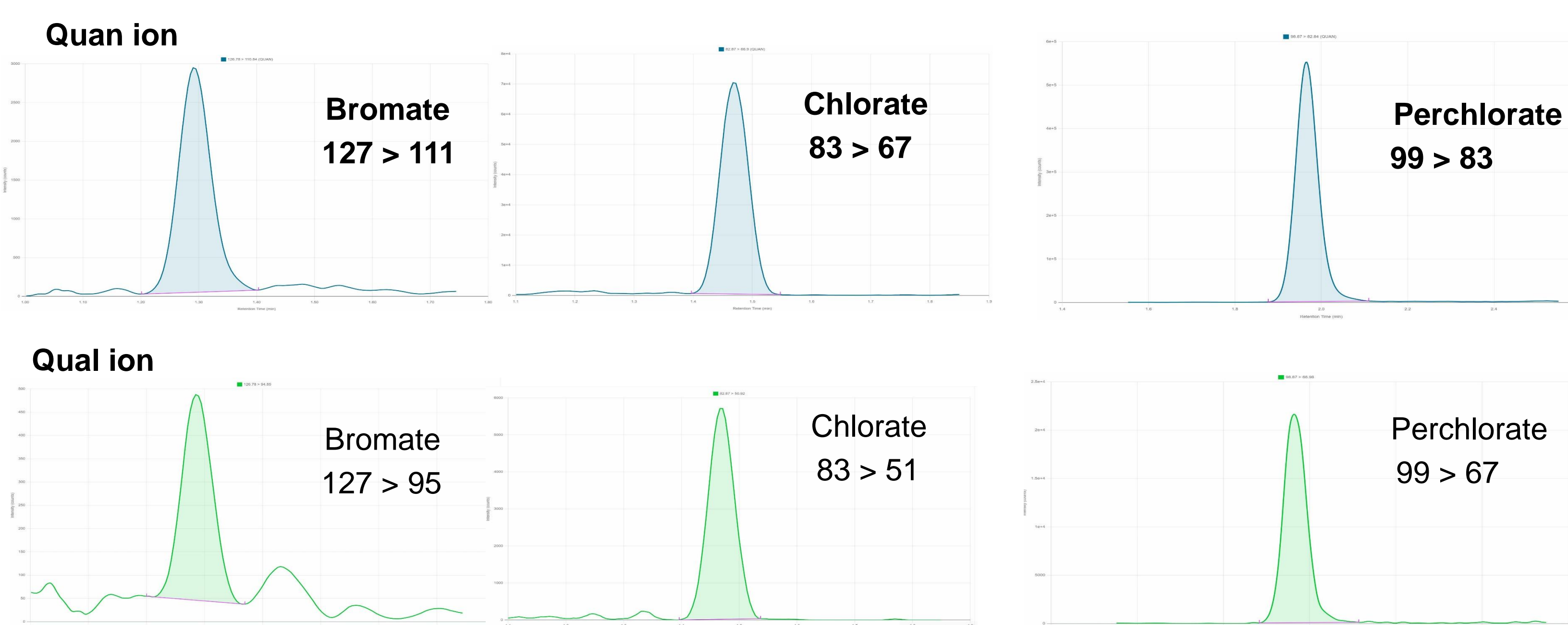


Figure 1. Chromatograms of chlorate, perchlorate and bromate from the analysis of matrix standards (infant formula) at 0.1 µg/kg.

Parameter	SANTE Criteria	Bromate	Chlorate	Perchlorate	Bromate	Chlorate	Perchlorate
		Infant formula			Cucumber		
Retention time (min)	± 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Ion ratio	± 30%	< 5%	< 13%	< 25%	< 6%	< 14%	< 25%
Residuals	± 20%	< 6%	< 6%	< 5%	< 6%	< 7%	< 6%

Table 3 : Summary of method parameters for chlorate, perchlorate and bromate in infant formula and cucumber.

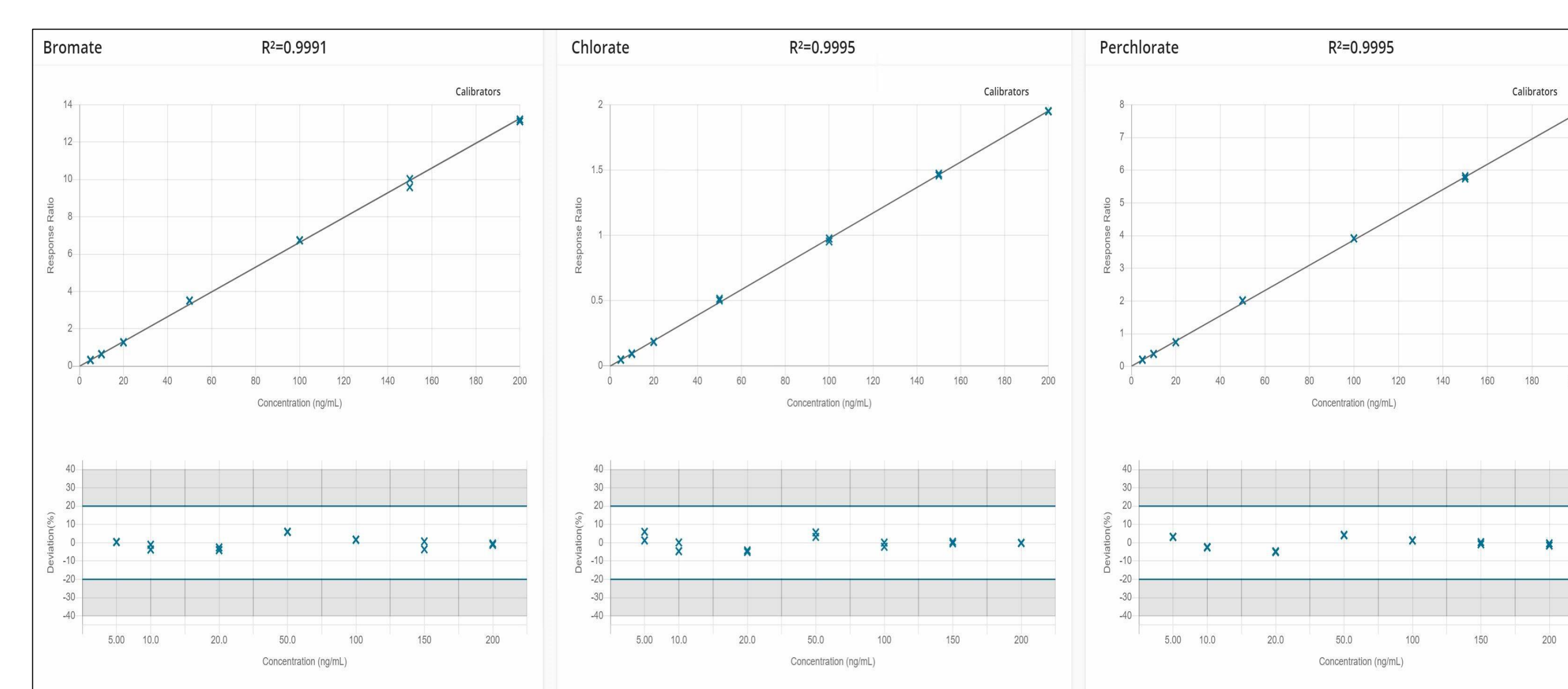


Figure 2. Calibration and residual plots for chlorate, perchlorate and bromate in infant formula (5 - 200 µg/kg).

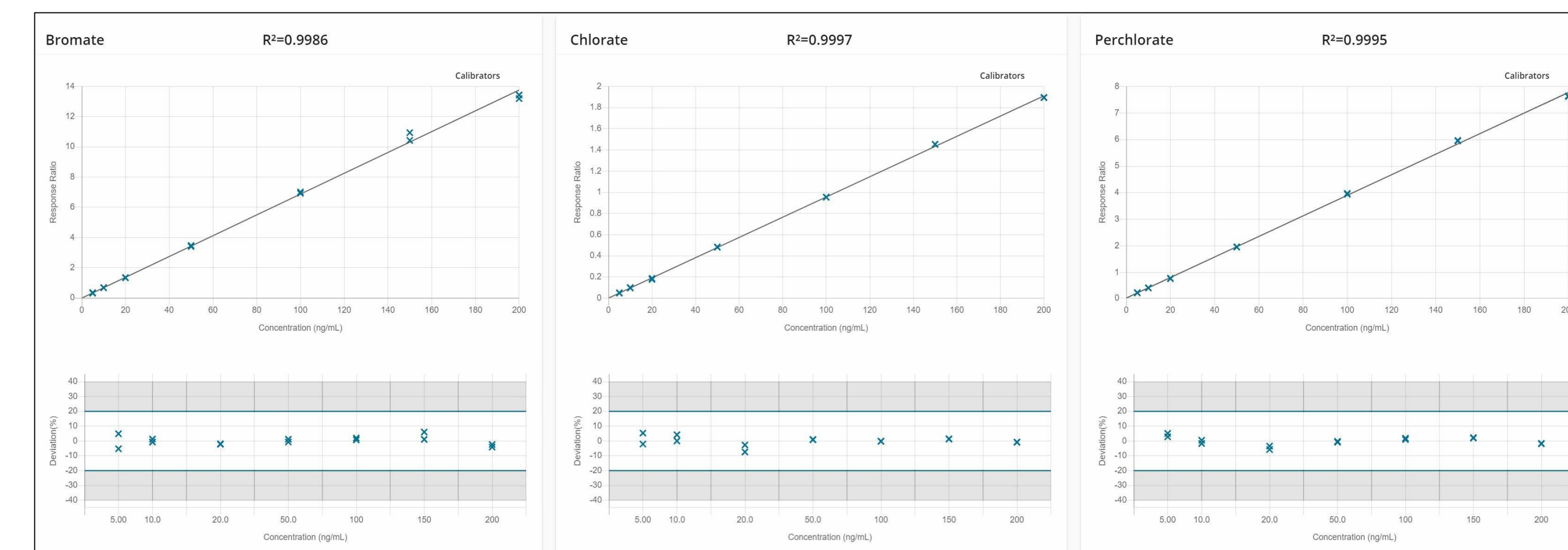


Figure 3. Calibration and residual plots for chlorate, perchlorate and bromate in cucumber (5 - 200 µg/kg).

CONCLUSION

- Excellent sensitivity (LOQ ≤ 0.1 µg/kg) has been achieved with the Xevo TQ Absolute MS System. This allows method flexibility to be realized when sample dilution or reduced sample injection volume is required. Excellent selectivity and retention have been achieved for the 3 analytes with the Atlantis Premier BEH C18 AX Column facilitated by the presence of anion exchange sites on the column.
- Method performance was successfully evaluated using matrix-matched standards prepared in cucumber and infant formula using the EURL Quick Polar Pesticides (QuPPE) PO and AO methods respectively. Response for the 3 compounds was linear over a range of 5 - 200 µg/kg with coefficients of determination (r²) > 0.99, retention times, ion ratios and residuals within the SANTE acceptance criteria.⁵

REFERENCES

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