Non-target High Throughput Screening Method for 765 Multigroup and Multiclass Pesticides and Chemical Contaminants in Fruits and Vegetables by GC/LC-Q-TOF/MS

The Early-Stage Preparation and Implementation Protocol

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1. Background

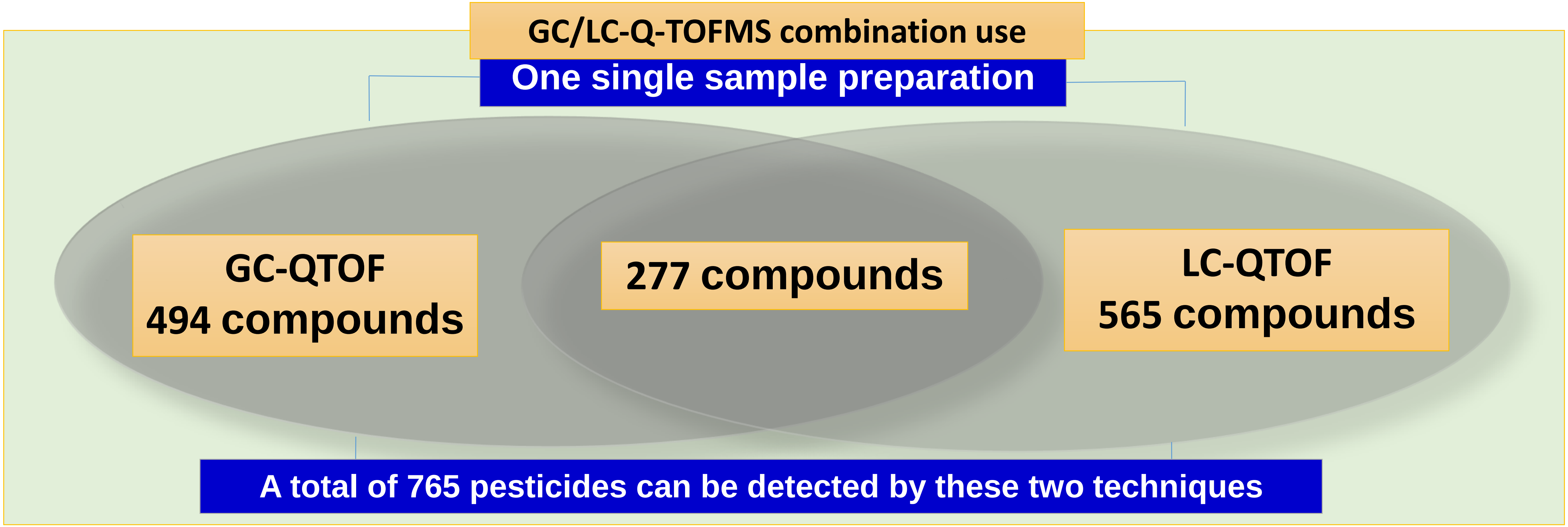
Our Lab's Journey with AOAC Official Methods（1994–2019）

Our 30-year pesticide residue analytical technique study is post-foreign trade serving-AOAC integrating oriented and has encompassed four stages of GC-LC-Low Resolution-High Resolution, and during the first three stages 3 AOAC standards were developed, and high-resolutoin MS technology is being studied in the fourth stage.

Since becoming a member of AOAC for 25 years, three AOAC Official Methods have been established.

2. The study of combination-use high-throughput analytical method of LC-Q-TOF/MS and GC-Q-TOF/MS

2.1 New method for determination of 765 pesticides in fruits and vegetables by the combination of the two technologies



Replacement of substantial standard with digital one as comparison
Frog-leap development from target detection ton non-target suspected screening

Realization of digitalization and informatization of pesticide residue analytical technology

2.2 Five elements of Electronic Standards for each pesticide

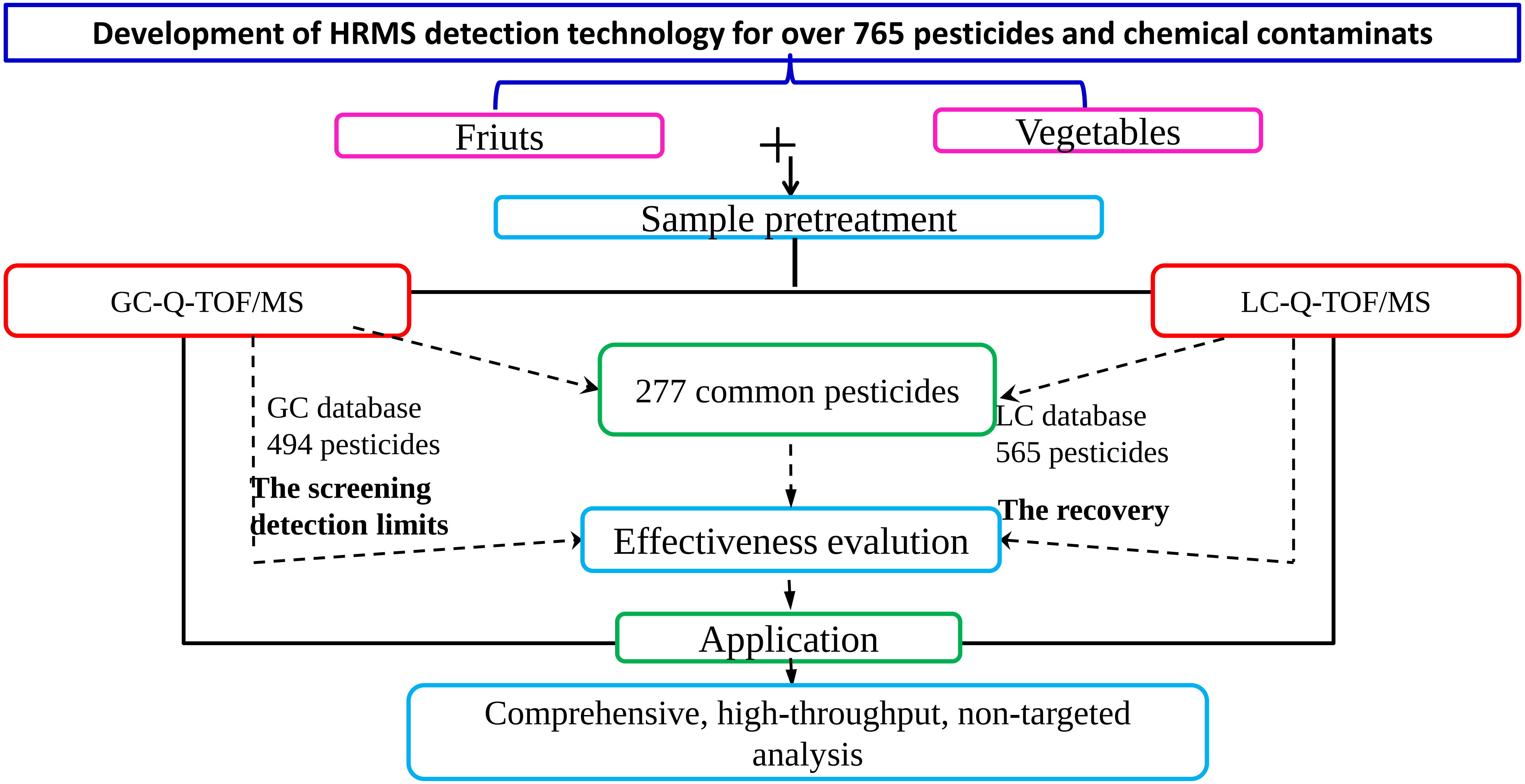
Through stduy, an independent digital identity card was developed for each of 765 pesticides commonly used in fruits and vegetables (digital standards equivalent to facial identifiation technology), hence the establishment of the new method of using digita standard to replace the substantial standard as comparison.

Elements of each pesticide electronic ID

- ① Retention time
- ② Accurate mass for molecular ion
- ③ Isotope distribution
- ④ Isotope abundance
- ⑤ Accurate MS/MS fragments and library

Meeting the requirement of EU SANTE/11813/2017 guidance document

2.3 High-resolution AOAC Method Flow Chart for 765 Pesticides in Fruits and Vegetables by GC/LC-Q-TOFMS



2.4 Fourth, six innovation technical indexes for the combination use of the two technology

6 updated technical indexes

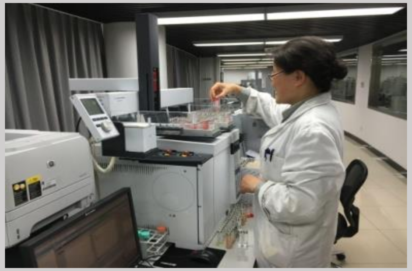
No	Indexes	LRMS (GC-MS/MS&LC-MS/MS)		HRMS (GC-Q-TOFMS&LC-Q-TOFMS)
1	quantitation/qualification	material standard	→	electronic standards
2	Monitor mode	Targeted	→	non-targeted
3	Detection mode	Divide into groups	→	Full scan
4	Pesticide Numbers	~200-300	→	Nearly 1000 (determined by both techniques)
5	Analysis time	4-8 h	→	0.5 h
6	Resolution	Unit Dalton	→	0.0001m/z

3. A probe into the “inventory” pesticide residues in fruits and vegetables available in China market

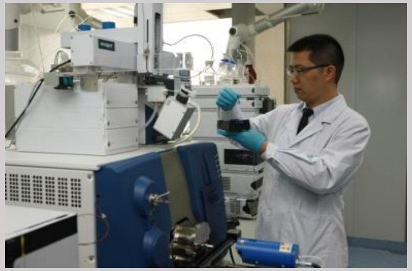
3.1 Devlopment of our national network coalition per five unified opeatioal procedures: unified sampling, unified preparation, unified determination, unified process and transfer the data, unified format of statistical report.

CAIQ

QingHuangDao CIQ



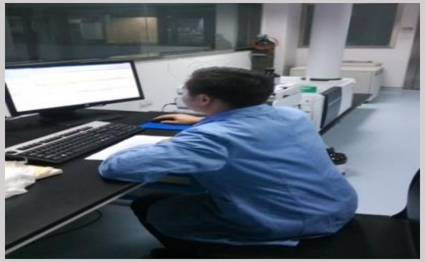
ShangHai CIQ



ShenZhen CIQ

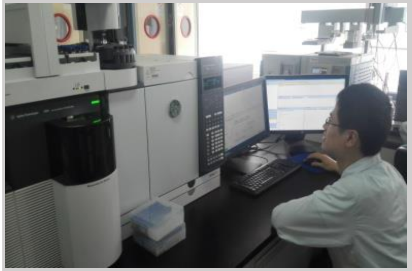
Beijing UniStar

AnHui CIQ

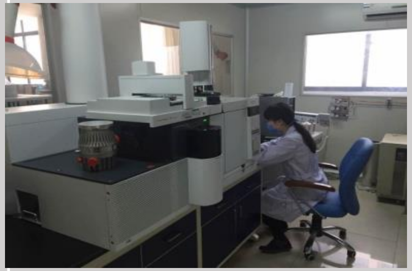


JiangXi CIQ

ShangDong CIQ



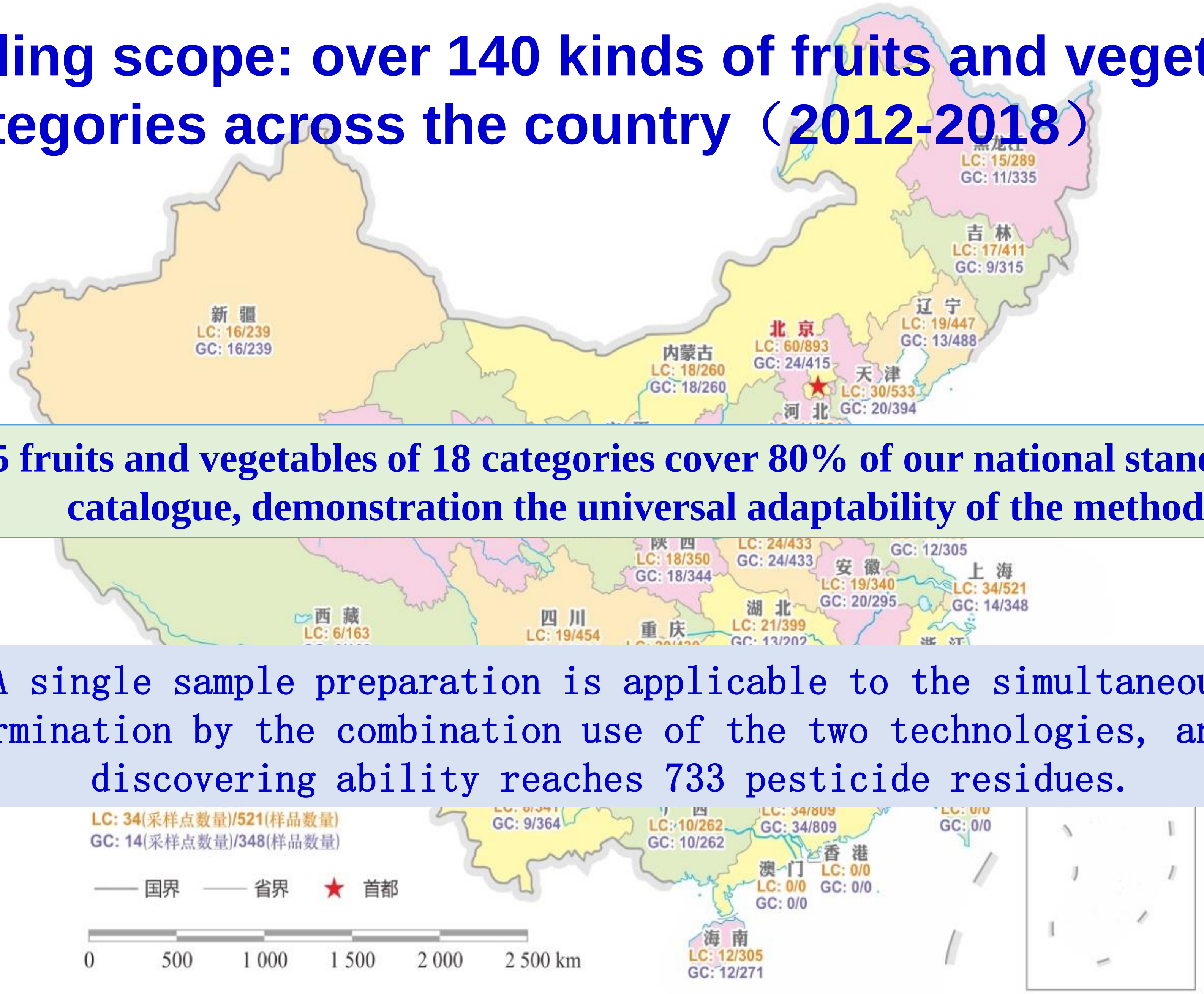
FuJian CIQ



NingXia CIQ

Allied labs run all-close, flight monitoring and data assuring, consisting of five features: representative, unified, completeness, safety and reliability

3.2 Sampling scope: over 140 kinds of fruits and vegetables of 18 categories across the country（2012-2018）



135 fruits and vegetables of 18 categories cover 80% of our national standard catalogue, demonstration the universal adaptability of the method

A single sample preparation is applicable to the simultaneous determination by the combination use of the two technologies, and the discovering ability reaches 733 pesticide residues.

3.3 Census of pesticides in market fruits and vegetables was made two times in 45 key cities across the country（2012-2019）

- **Pessticide residues are universally present in the market fruits, vegetables and tea across the country.**

- **The census of pestcide residues in 40000 lots of fruits and vegetable samples across 31 provincial capitals/cities directly under the Central Government indicated a frequent detection 533 pesticides for 115981 times, and 45 cities have a 12.2% detection of samples with 76 high toxicity and forbidden pesticides.**
- **A total of 454 pesticides for 41951 times have been detected and 67 pesticides of high toxicity have been found for 3986 times in the census of 4944 pesticide residues for 7 kinds of tea samples at over 360 sampling spots across 31 provincial capitals/cities directly under the Central Government, reflecting that that pesticide residues in the market fruits, vegetables and teas of our country are universally present, and the situation looks optimistic by no means.**

a total of 660 pesticides have been found,
and the frequencies of detection were 53549

4. Complementation and strong detection capability by combination of GC/LC-Q-TOFMS

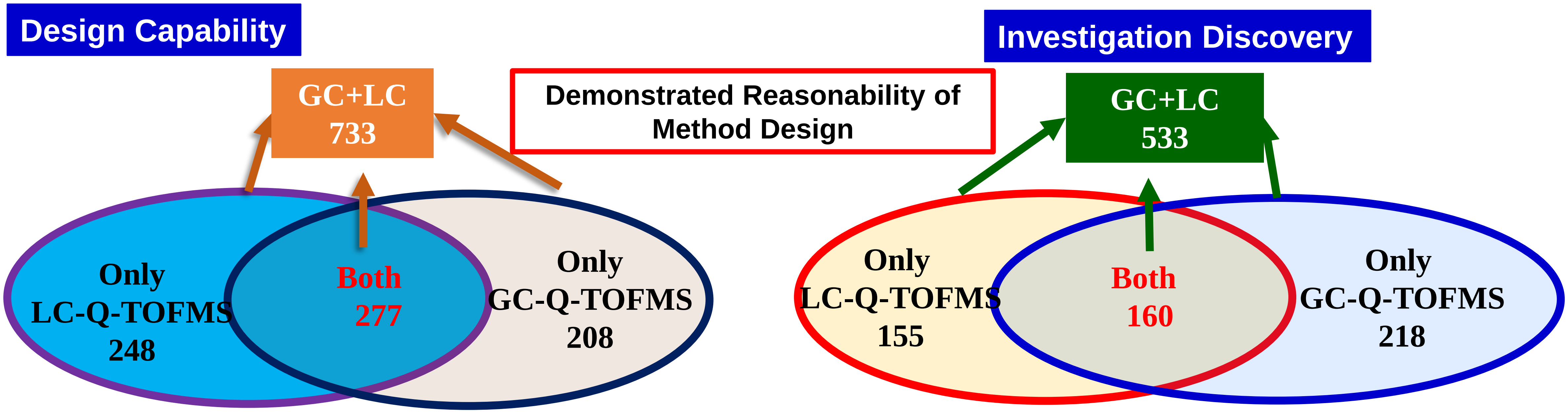
4.1 the detection capability has increased with the combination use technologies in comparison with the single use technology

Design Capability 733 Pesticides

LC+GC	LC	GC	Only LC	Only GC	Both
733	525	485	248	208	277

Actual discovery: 533 pesticides

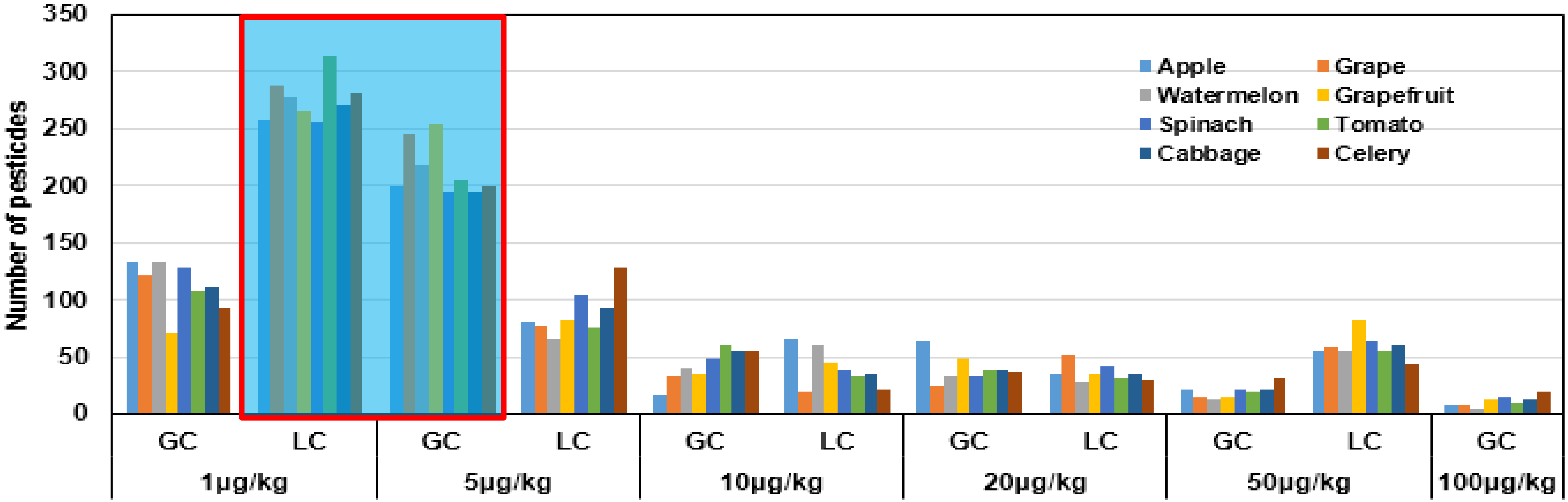
LC+GC	LC	GC	Only LC	Only GC	Both
533	315	378	155	218	160



There are ~ 30% capacity that has not been detected yet.

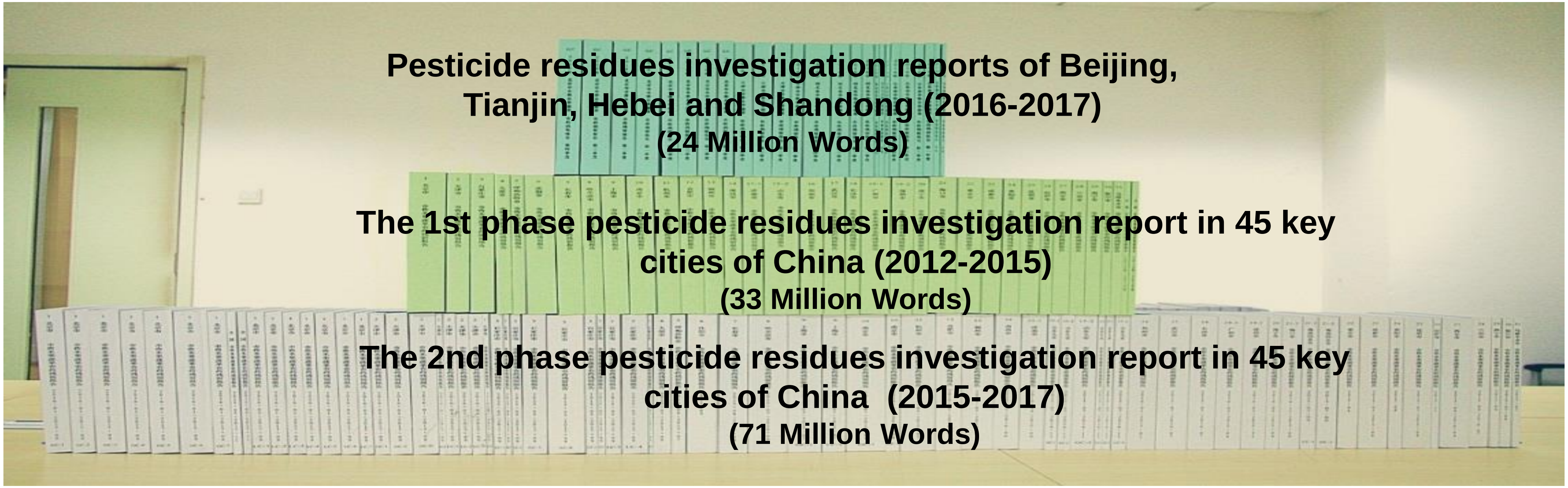
4.2 The combination use is complimentary with their advantages, which has increased the sensitivity of the method and obviously improved the assurance of international uniform standard 10ug/kg screening.

LC has its unqiue advantage with 1 ug/kg screening limt, while GC has the same advantage with 5 ug/kg. The combination use of the two is complimentary with each other, which may increase the sensitivity of the method markedly and greatly improve the assuraing ability of international uniform stand 10 ug/kg accurate quantification.



4.3 Residue report of two-term census from 31 provincial capitals/ cities under the Central government 2012-2017

The big data report covers 40000 lots of market fruits and vegetables at 1500 sampling spots nationwide, with a detection of 533 pesticides for 115981 times, and 0.32 billion spectra has been obtained.



2012-2017 (2-Phase Investigation) Pesticide Residues Reports (104 Million Words)

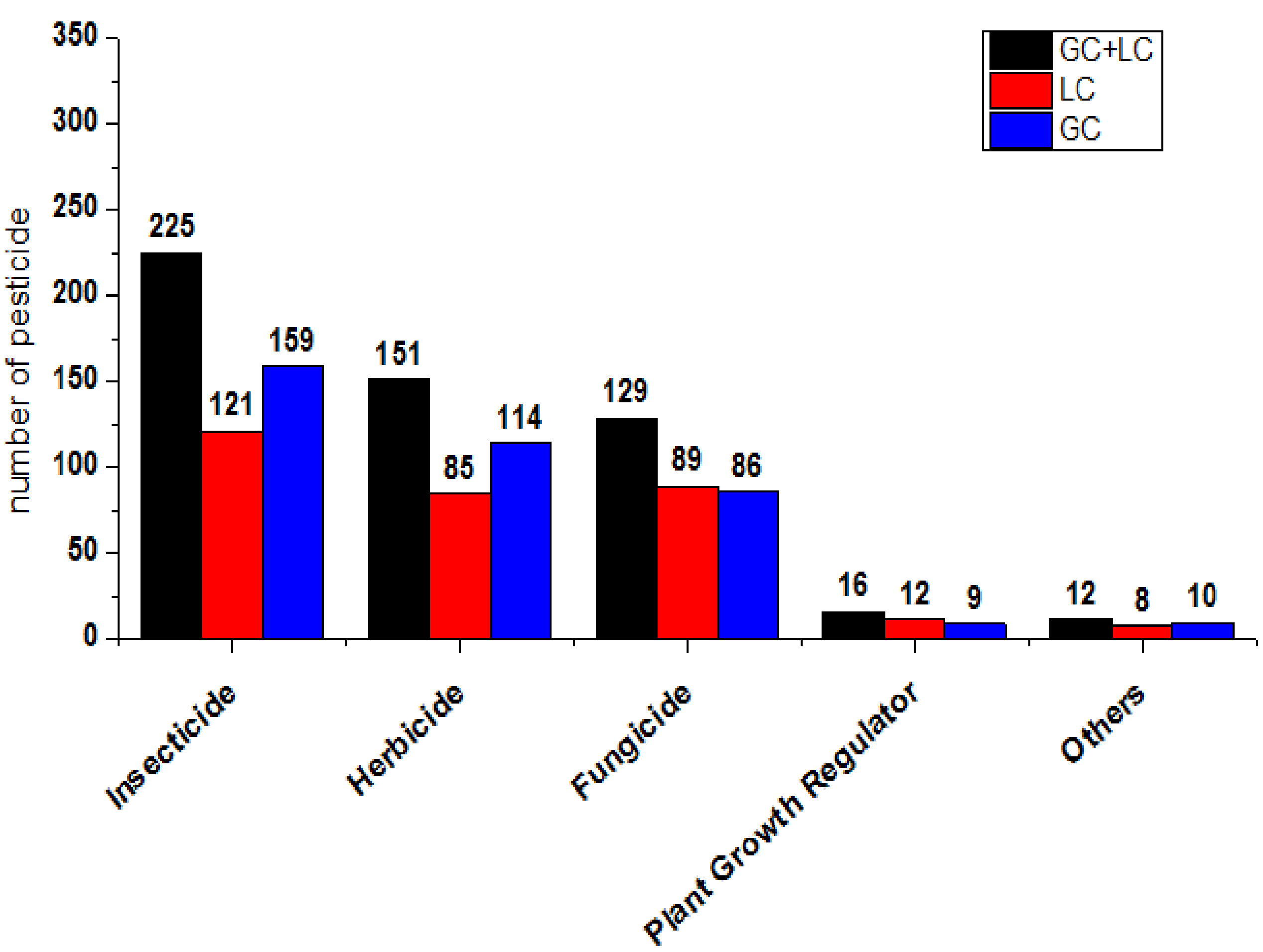
These data are valuable treasure in food safety and human health

4.4 The census finds that the pesticides applied in China are of multi-varieties and multi-categories.

(1) Classification by Function

Investigation Discovery (533 pesticides) (2012-2017)

Function	LC+GC	LC	GC	Only LC	Only GC	Both
Insecticide	225	121	159	66	104	55
Herbicide	151	85	114	37	66	48
Fungicide	129	89	86	43	40	46
Plant Growth Regulator	16	12	9	7	4	5
Others	12	8	10	2	4	6
Total	533	315	378	155	218	160



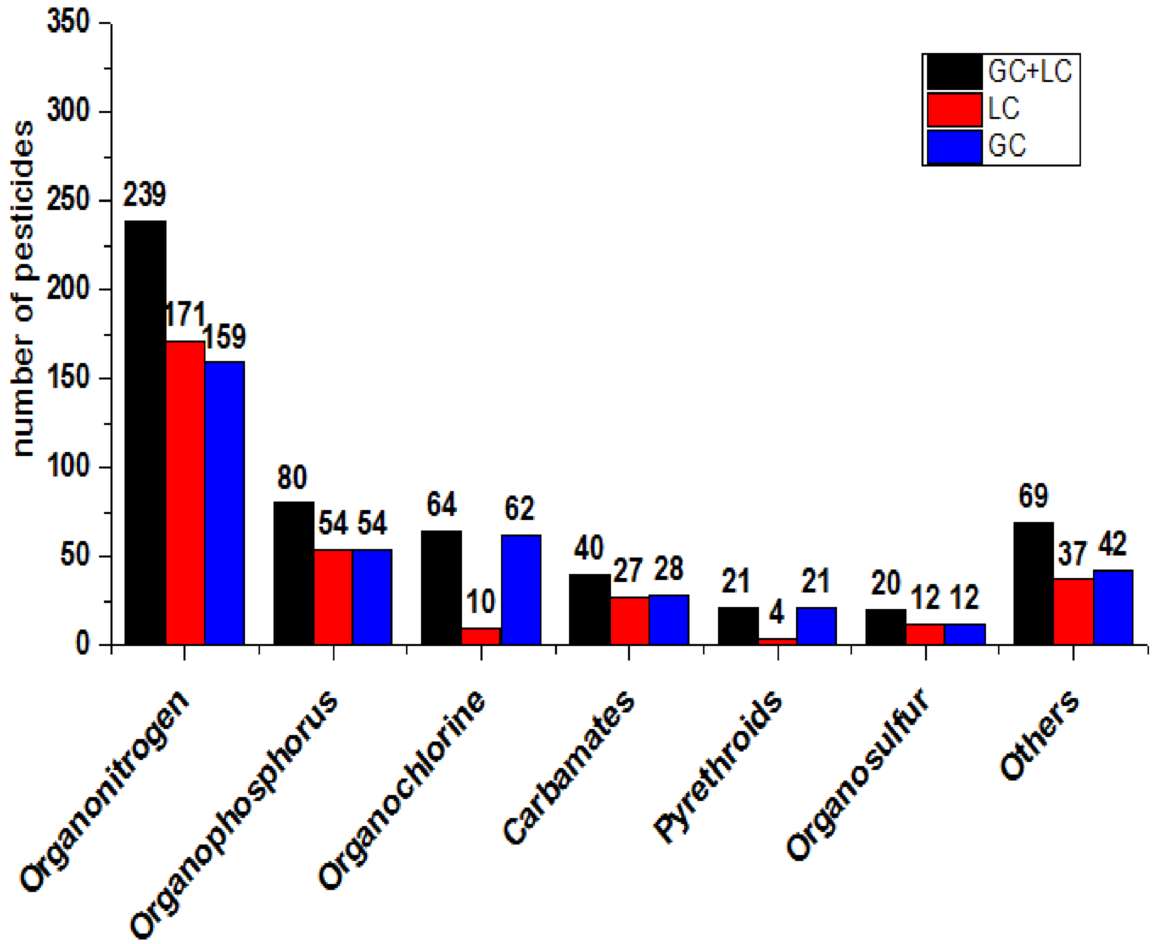
Classification by Function , nowadays Insecticides, Herbicides and Fungicides are the top three types pesticides used in China.

4.4 The census finds that the pesticides applied in China are of multi-varieties and multi-categories.

(2) Classification by Compound

Investigation Discovery (533 pesticides) (2012-2017)

Compound	LC+GC	LC	GC	Only LC	Only GC	Both
Organonitrogen	239	171	159	80	68	91
Organophosphorus	80	54	54	26	26	28
Organochlorine	64	10	62	2	54	8
Carbamates	40	27	28	12	13	15
Pyrethroids	21	4	21	0	17	4
Organosulfur	20	12	12	8	8	4
Others	69	37	42	27	32	10
Total	533	315	378	155	218	160



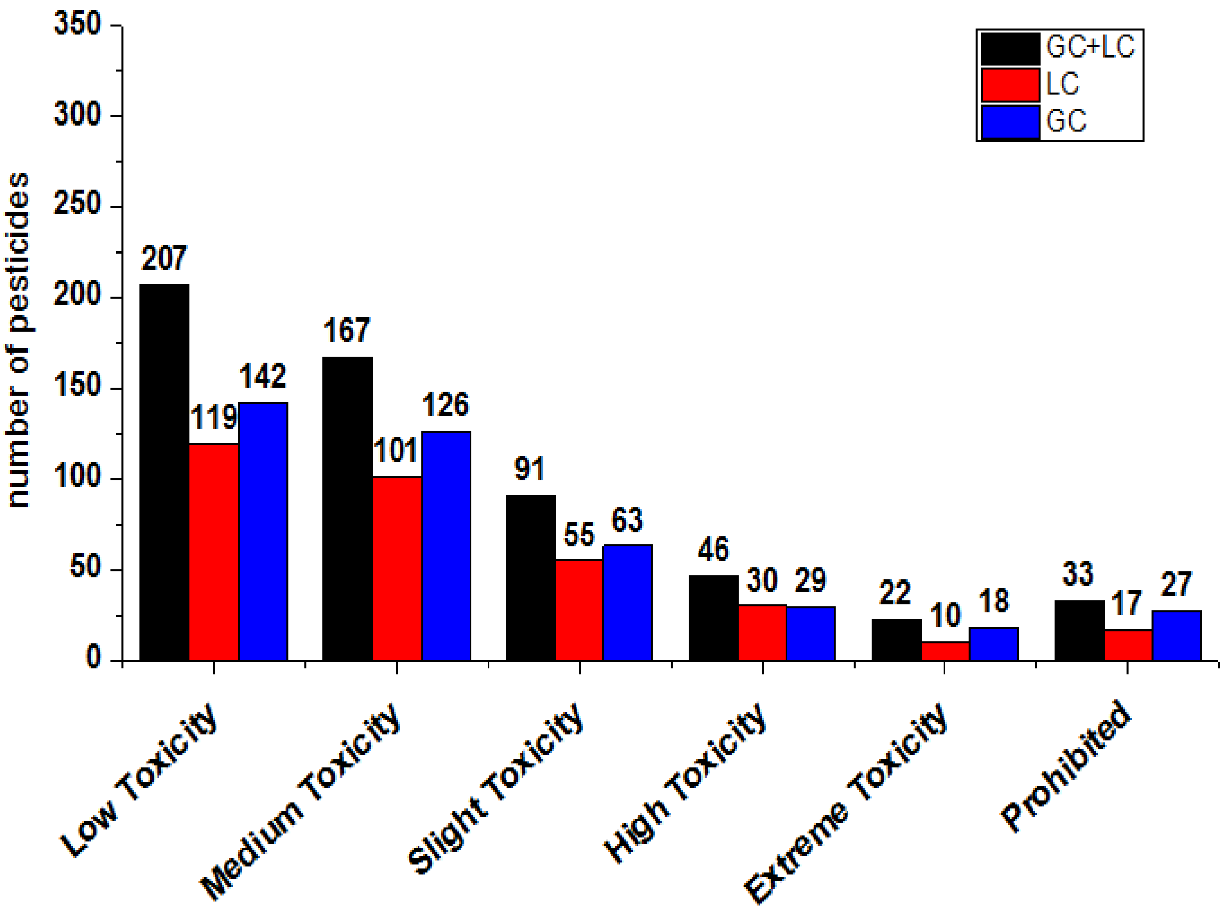
Classification by compound, nowadays Organonitrogen, Organophosphorus and Organochlorine pesticides were the top three classes used in China.

4.4 The census finds that the pesticides applied in China are of multi-varieties and multi-categories.

(3) Classification by Toxicity

Investigation Discovery (533 pesticides) (2012-2017)

Toxicity	LC+GC	LC	GC	Only LC	Only GC	Both
Low Toxicity	207	119	142	65	88	54
Medium Toxicity	167	101	126	41	66	60
Slight Toxicity	91	55	63	28	36	27
High Toxicity	46	30	29	17	16	13
Extreme Toxicity	22	10	18	4	12	6
Total	533	315	378	155	218	160
Prohibited	33	17	27	6	16	11



Classification by toxicity, nowadays the pesticides applied in China are mainly medium, low and slightly toxic pesticides.

4.5 EU Proficiency Test Further Demonstrate the Reliability of the Developed Method-2019

4.5.1 EU Proficiency Test –SM11

EUPT-SM11 Proficiency test Result

						CAIQ-Hezhong (Lab 020)			
No	**Pesticides Name**	**LQ group**	**GQ group**	**Robust Mean**	**CV (%)**	**Meas. (mg/kg)**	**Z Score (Mean)**	**Instrument**	**Result from other — TOF**
1	Bifenazate	LQ-1-3	GQ-1-4	0.037	44.9	0.025	-1.3	GC-Q-TOF	0.0067
2	Bifenazate diazene			0.031	46.2				
3	Etoxazole	LQ-2-3	GQ-2-2	0.060	20.7	0.0661	0.4	LC-Q-TOF	0.0699
4	Fenpyrazamine	LQ-1-5	GQ-2-4	0.052	17.2	0.0494	-0.2	LC-Q-TOF	0.0812
5	Flubendiamide	LQ-1-1		0.065	22.8	0.0526	-0.8	LC-Q-TOF	
6	Flufenacet	LQ-2-3	GQ-1-3	0.085	21.1	0.1328	2.2	GC-Q-TOF	0.1639
7	Fluopicolide	LQ-2-1		0.084	19.5	0.0902	0.3	LC-Q-TOF	
8	Isoprothiolane	LQ-2-1	GQ-1-2	0.067	18.5	0.0758	0.5	LC-Q-TOF	0.0789
9	Isopyrazam	LQ-1-1	GQ-2-4	0.057	22.0	0.0681	0.8	LC-Q-TOF	0.0815
10	Metrafenone	LQ-2-1		0.064	20.8	0.0639	0.0	LC-Q-TOF	
11	Orthosulfamuron	LQ-2-5		0.119	79.8	0.1487	1.0	LC-Q-TOF	
13	Penthiopyrad	LQ-1-2	GQ-2-3	0.054	17.9	0.0603	0.5	LC-Q-TOF	0.0636
14	Propoxur	LQ-2-4	GQ-1-3	0.081	18.1	0.0951	0.7	LC-Q-TOF	0.075
15	Pyridalyl	LQ-2-4	GQ-1-3	0.041	12.9	0.0421	0.1	GC-Q-TOF	0.0411
16	Spinetoram	LQ-2-2		0.052	35.1	0.046	-0.5	LC-Q-TOF	
17	Tricyclazole	LQ-2-2	GQ-1-1	0.082	15.2	0.112	1.5	GC-Q-TOF	0.0663
18	Valifenalate	LQ-1-纯品		0.043	20.2	0.0409	-0.2	LC-Q-TOF	

- EUPT-SM proficiency test is more challenging comparing to EUPT-FV. The organizer does not provide any target list and it belongs complete blind screening.
- For the EUPT-SM11 test of 2019, there are totally 17 pesticides spiked into the matrices. Bifenazate diazene belongs to metabolites and is not counted for evaluation. Totally 16 pesticides are evaluated.
- Totally, 22 laboratories reported 16 pesticides, and CAIQ-Hezhong is one of them.

4.5.2 EU Proficiency Test-FV21 Test

A-class lab	need to detect over 90% of pesticides to be evaluated with no false positive

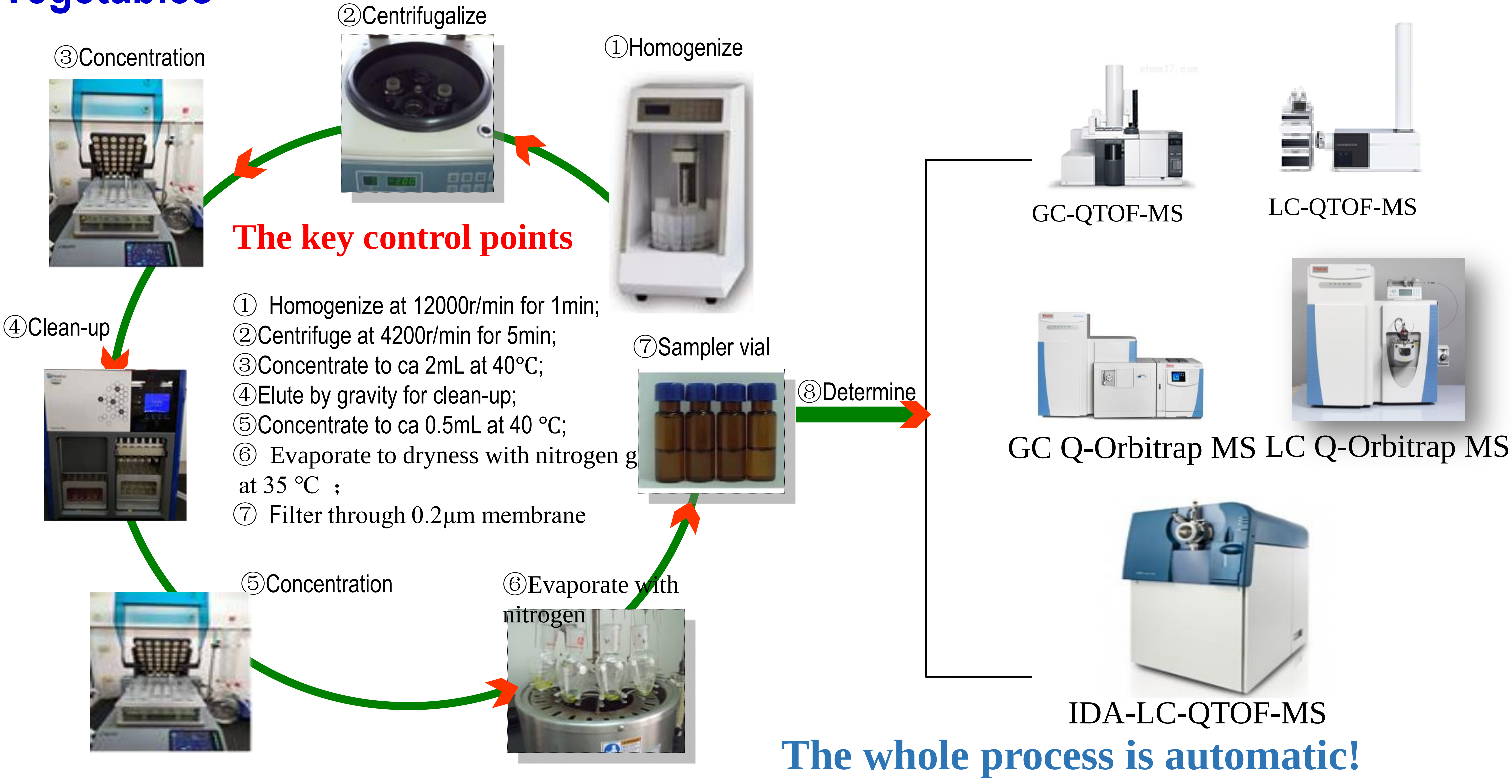
$\lvert z \rvert \le 2$	Acceptable	$AZ^2 \le 2$	Good
$2 < \lvert z \rvert < 3$	Questionable	$2 < AZ^2 < 3$	Satisfactory
$\lvert z \rvert \ge 3$	Unacceptable	$AZ^2 \ge 3$	Unsatisfactory

EUPT-FV21 Proficiency test Result AZ^2 0.35

									合众恒星 (Lab 642)				
序号	农药英文名称	LQ分组	GQ分组	Robust Mean 稳健平均值	CV (%) 变异系数	中位值	最大值	最小值	检测结果 (mg/kg)	Z Score	上报设备	回收率 (%)	另一TOF 结果
1	Acetamiprid	LQ-1-3		0.174	13.0	0.1710	0.3480	0.0640	0.151	-0.5	LC-Q-TOF	103	
2	Chlorantraniliprole	LQ-1-3		0.136	15.2	0.1330	0.7900	0.0804	0.116	-0.6	LC-Q-TOF	91	
3	Chlorpropham		GQ-1-1	0.084	14.0	0.0840	0.2050	0.0420	0.0676	-0.8	GC-Q-TOF	102	
4	Chlorpyrifos	LQ-1-3	GQ-2-1	0.051	17.6	0.0508	0.0920	0.0130	0.0408	-0.8	GC-Q-TOF	88	0.0406
5	Clothianidin	LQ-1-3		0.052	15.5	0.0520	0.1020	0.0290	0.0481	-0.3	LC-Q-TOF	111	
6	Diazinon	LQ-1-1	GQ-2-1	0.077	15.3	0.0769	0.5700	0.0320	0.0645	-0.6	GC-Q-TOF	97	0.0597
7	Difenoconazole	LQ-1-3	GQ-2-1	0.169	17.2	0.1670	3.0400	0.0000	0.1327	-0.9	LC-Q-TOF	89	0.1282
8	Dimethoate	LQ-1-2	GQ-1-2	0.124	13.0	0.1240	1.0160	0.0230	0.1053	-0.6	LC-Q-TOF	104	0.098
9	Fenamidone	LQ-1-3	GQ-2-3	0.615	15.2	0.6090	1.3000	0.3480	0.6016	-0.1	LC-Q-TOF	95	0.5334
10	Fluxapyroxad	LQ-1-1	GQ-2-3	0.536	12.4	0.5310	1.2520	0.3400	0.5156	-0.2	LC-Q-TOF	95	0.4264
11	Metaflumizone	LQ-1-4		0.210	23.6	0.2020	0.4560	0.0900	0.1527	-1.1	LC-Q-TOF	92	
12	Omethoate	LQ-2-1	GQ-2-1	0.008	22.3	0.0080	0.0600	0.0028	0.0069		LC-Q-TOF	99	
13	Propamocarb	LQ-2-2	GQ-2-1	0.170	17.8	0.1700	0.9370	0.0210	0.1671	-0.1	LC-Q-TOF	85	
14	Propyzamide	LQ-2-2	GQ-2-2	0.083	15.0	0.0824	0.1590	0.0390	0.071	-0.6	LC-Q-TOF	94	0.0715
15	Pyraclostrobin	LQ-1-6	GQ-1-4	0.076	15.2	0.0750	0.1640	0.0280	0.0668	-0.5	LC-Q-TOF	76	
16	Teflubenzuron	LQ-2-1	GQ-1-4	0.110	18.4	0.1080	0.4520	0.0546	0.0932	-0.6	GC-Q-TOF	104	0.0941
17	Trifloxystrobin	LQ-1-1	GQ-1-4	0.230	13.4	0.2300	0.6140	0.1310	0.217	-0.2	LC-Q-TOF	84	0.1863
18	Triflumuron	LQ-2-3		0.469	17.3	0.4600	1.1920	0.0800	0.436	-0.3	LC-Q-TOF	100	
19	Penthiopyrad	LQ-1-2	GQ-2-3	0.223	12.4	0.2240	0.4510	0.1490	0.2164	-0.1	LC-Q-TOF	94	0.1936
20	Spinetoram	LQ-2-2		0.056	21.6	0.0541	0.1150	0.0310	0.0531	-0.2	LC-Q-TOF	90	
21	Tritosulfuron	LQ-1-6		0.066	19.7	0.0659	0.0890	0.0000	0.0538	-0.7	LC-Q-TOF	97	

- For the EUPT-FV test, there are total 21 pesticides spiked, with 18 coming from the target list of 205 pesticides, and 3 from voluntary list of 34 pesticides. Among them, 3 from voluntary list and omethoate are not counted for evaluation. The pesticides to be evaluated are 17.
- It is reported that 28 labs detected total 21 pesticides and 90 labs detected all 18 pesticides in the target list.
- CAIQ-Hezhong detected all 21 pesticides with no false positive and $AZ^2 \le 2$, belonging to Class A laboratories.
- The results from CAIQ-Hezhong are all from QTOF. For those pesticides detected by both LC/QTOF and GC/QTOF, the results are also consistent.

5.1 Flow chart of AOAC method study for 765 pesticide residues In fruits and vegetables



5.3 "Shrunken" AOAC collaborative study protocol (AOAC Official Method 2014.09 AOAC study is conducted per this version).

To organize an inter-collaborative study on several hundreds of pesticides, it will bring unimaginalbe difficulties such as resources, time and personnel to the participants. Therefore, an abriged version is proposed.

1) Selection of two kinds of fruits: apple and grapes; and two types of vegetables: tomatoes and cabbages
2) Both GC-Q-TOF/MS and LC-Q-TOF/MS are adopted to detect 20 pesticides respectively, with a total of 40 pesticides for the collaborative study.

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5.4 First step, optimum selection of 90 pesticides

No	Pesticide Source	Selected Pesticides			Total
		Initial	Middle	Final	
1	GC/LC-QTOF-MS High Throughput Screening-765 Pesticides, Co-detectable- 457 Pesticides	Pesticides that can be verified by both techniques in three spiked level	124	58	90
2	EUPT FV-18、FV-19&FV-20, Total 229 pesticides involved	174 pesticides could be detected in our lab	72	56	
3	AOAC Official Method for Pesticides in Teas 625 Pesticides involved	Detectable by both techniques	201	38	

5.5 List of stability study of 90 pesticides

序号	农药	CAS号	序号	农药	CAS号	序号	农药	CAS号
1	Tebuconazole	107534-96-3	31	Fenthion	55-38-9	61	Desmetryn	1014-69-3
2	Mepanipyrim	110235-47-7	32	Ethion	563-12-2	62	Diphenamid	957-51-7
3	Tetraconazole	112281-77-3	33	Tolclofos-methyl	57018-04-9	63	Methoprotryne	841-06-5
4	Tebufenpyrad	119168-77-3	34	Metalaxyl	57837-19-1	64	Propisochlor	86763-47-5
5	Fenazaquin	120928-09-8	35	Terbuthylazine	5915-41-3	65	Sebuthylazine	7286-69-3
6	Cyprodinil	121552-61-2	36	Fenarimol	60168-88-9	66	Simeton	673-04-1
7	Malathion	121-75-5	37	Dimethoate	60-51-5	67	Dimethenamid	87674-68-8
8	Quinoxyfen	124495-18-7	38	Carbaryl	63-25-2	68	Atrazine	1912-24-9
9	Azoxystrobin	131860-33-8	39	Fluopyram	658066-35-4	69	Ametryn	834-12-8
10	Ethoprophos	13194-48-4	40	Penconazole	66246-88-6	70	Simeconazole	149508-90-7
11	Iprovalicarb	140923-17-7	41	Flutolanil	66332-96-5	71	Thiazopyr	117718-60-2
12	Trifloxystrobin	141517-21-7	42	Buprofezin	69327-76-0	72	Heptenophos	23560-59-0
13	Kresoxim-methyl	143390-89-0	43	Flutriafol	76674-21-0	73	Isazofos	42509-80-8
14	Spirodiclofen	148477-71-8	44	Paclobutrazole	76738-62-0	74	Thionazin	297-97-2
15	Carbofuran	1563-66-2	45	Clomazone	81777-89-1	75	Sulfotep	3689-24-5
16	Fenamidone	161326-34-7	46	Diniconazole	83657-24-3	76	Quinalphos	13593-03-8
17	Fenamiphos	22224-92-6	47	Flusilazole	85509-19-9	77	Tebupirimfos	96182-53-5
18	Phosalone	2310-17-0	48	Myclobutanil	88671-89-0	78	Pentanochlor	2307-68-8
19	Pirimicarb	23103-98-2	49	Cadusafos	95465-99-9	79	Metolachlor	51218-45-2
20	Propyzamide	23950-58-5	50	Pyriproxyfen	95737-68-1	80	Orbencarb	34622-58-7
21	Triazophos	24017-47-8	51	Pyridaben	96489-71-3	81	Pyributicarb	88678-67-5
22	Phenthoate	2597/3/7	52	Benalaxyl	71626-11-4	82	Esprocarb	85785-20-2
23	Chlorpyrifos	2921-88-2	53	Fluxapyroxad	907204-31-3	83	Promecarb	2631-37-0
24	Pirimiphos-methyl	29232-93-7	54	Tetramethrin	7696-12-0	84	Fenothiocarb	62850-32-2
25	Profenofos	41198-08-7	55	Cyflufenamid	180409-60-3	85	Benzoylprop-ethyl	22212-55-1
26	Bupirimate	41483-43-6	56	Tricyclazole	41814-78-2	86	Diethatyl-ethyl	38727-55-8
27	Isoprothiolane	50512-35-1	57	Flurprimidol	56425-91-3	87	Indoxacarb	144171-61-9
28	Pyrimethanil	53112-28-0	58	Picoxystrobin	117428-22-5	88	Butralin	33629-47-9
29	Bitertanol	55179-31-2	59	Piperonyl Butoxide	1951/3/6	89	Acetochlor	34256-82-1
30	Triadimenol	55219-65-3	60	Atrazine-Desethyl	6190-65-4	90	Triadimefon	43121-43-3

5.6 The 90 pesticides stability study in four frozen FV matrices

- **Matrix selection**

4 matrices: apples, grapes, tomatoes and cabbages （Method validation completed in December 2018）

- **Fortified concentration**

two initial fortified concentrations for each matrix ;

Quantification mode: single-point quantification ;

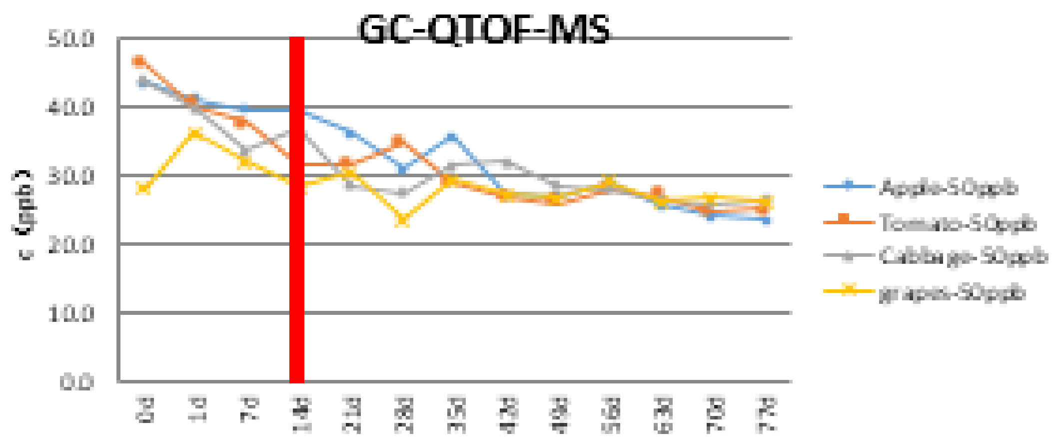
- **Test protocol of pesticides stability study for 3 months**

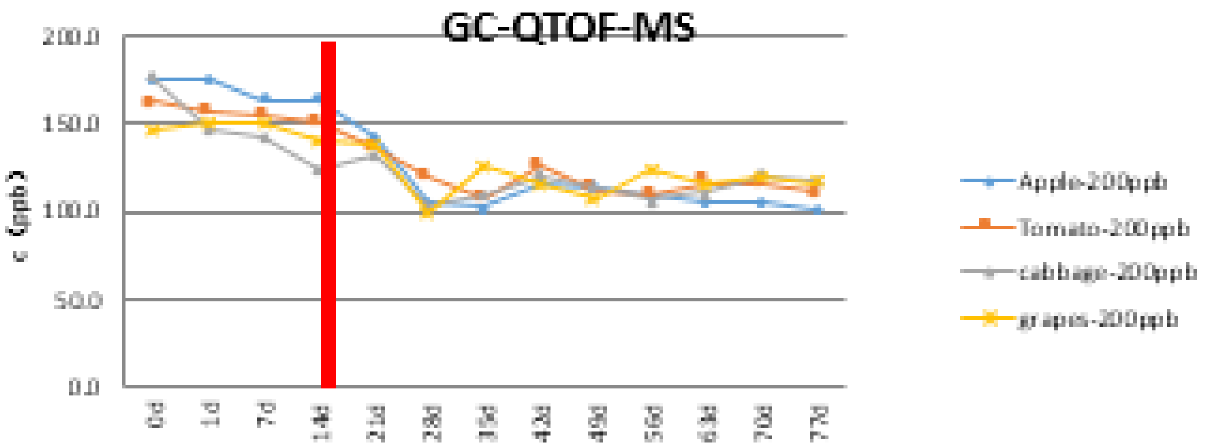
Analyze the degradation concentrations of the 13 time to obtain two instrument*4 matrices*90 pesticides*2 concentrations （50 and 200 μg/kg） *6 parallels*13 determinations=112320 data

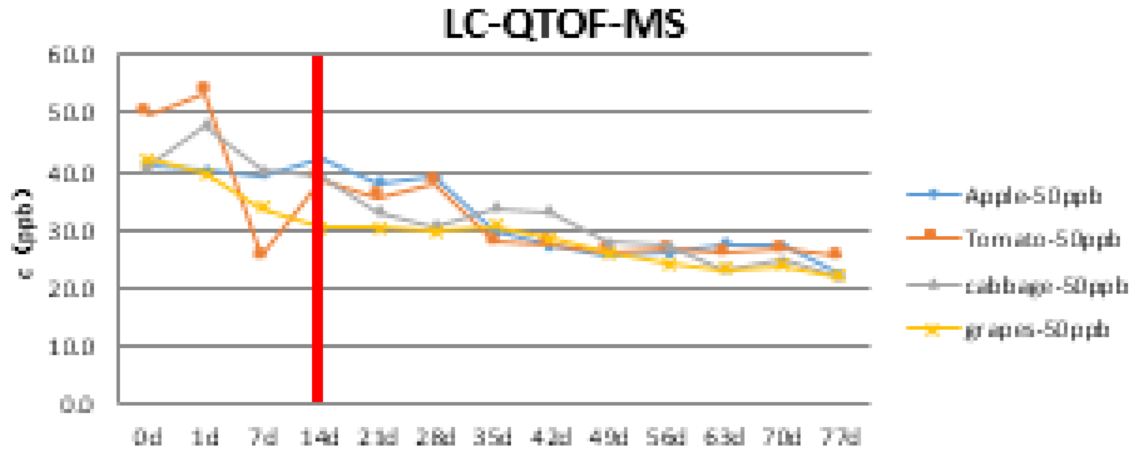
- **Raw data and summarized analysis**

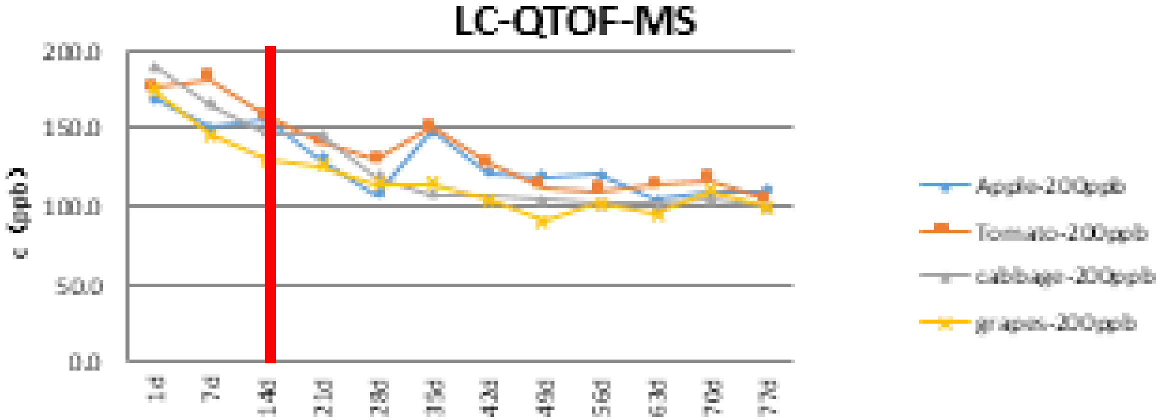
Average the 6 parallels measured every day, and give out the average summarized data of the measured results on different days for 90 pesticides with two instrument, four matrices and two fortified concentration levels.

5.7 Degradation curves for GC/LC-QTOF-MS









For apples, grapes, tomatoes and cabbages， Observe it after adding the standards from 0、1、7、14、21、28、35、42、49、56、63、70 and 77 within the recent three months (totaling 13 times) and draw a degradation curve, giving out the fitted equation and correlation coefficients.

5.8 The top 20 pesticide were selected according to the degradation curves of 90 pesticides (LC-Q-TOF/MS)

RSD of the original concentration of 20 pesticides in 14-77 days(%)

No.	Name	Apple		Grape		Cabbage		Tomato	
		50ppb	200ppb	50ppb	200ppb	50ppb	200ppb	50ppb	200ppb
1	Acetochlor	19.8	15.3	11.0	8.9	16.7	11.1	38.5	13.2
2	Ametryn	24.7	14.7	10.3	12.6	20.8	12.0	16.5	13.0
3	Benalaxyl	16.6	17.1	11.8	13.7	18.2	16.2	15.5	12.8
4	Diphenamid	22.0	10.3	12.8	14.9	16.6	11.6	18.9	9.9
5	Esprocarb	16.5	16.3	14.8	9.3	17.7	17.1	28.3	11.7
6	Fenothiocarb	18.5	16.0	13.3	[illegible]	21.0	16.3	17.2	11.9
7	Mepanipyrim	20.6	16.7	12.6	11.8	15.3	11.5	17.9	14.9
8	Metalaxyl	[illegible]	12.0	11.4	10.9	18.1	14.8	18.8	13.5
9	Methoprotryne	22.1	13.5	16.7	13.8	22.2	12.5	18.2	12.9
10	Metolachlor	21.0	13.4	11.2	14.7	17.5	15.1	24.8	10.5
11	Orbencarb	21.6	14.4	15.4	10.8	17.3	14.4	38.6	11.0
12	Pentanochlor	18.6	17.6	13.5	13.1	18.0	14.2	22.5	14.9
13	Picoxystrobin	22.1	17.5	17.8	11.1	14.9	11.6	17.5	13.3
14	Pirimiphos-methyl	17.5	15.3	8.8	9.5	17.0	12.3	24.5	9.3
15	Propisochlor	24.0	16.5	15.3	10.4	21.8	15.2	40.0	14.9
16	Quinalphos	21.5	18.5	13.6	15.7	20.8	17.3	19.1	13.5
17	Sebuthylazine	24.7	13.2	22.9	12.8	16.0	11.5	16.2	12.8
18	Simeton	28.9	11.6	12.4	13.5	17.9	13.2	18.9	12.5
19	Terbuthylazine	27.8	16.1	14.9	9.4	16.0	12.1	18.0	13.5
20	Tetraconazole	29.7	17.6	15.0	18.7	17.6	15.9	14.5	13.0

The top 20 pesticide in stability were selected according to the degradation curves of 90 pesticides.

5.9 The top 20 pesticide were selected according to the degradation curves of 90 pesticides (GC-Q-TOF/MS)

RSD of the original concentration of 20 pesticides in 14-77 days(%)

No.	Name	Apple		Grape		Cabbage		Tomato	
		50ppb	200ppb	50ppb	200ppb	50ppb	200ppb	50ppb	200ppb
1	Ametryn	17.4	17.5	6.0	8.8	11.2	9.6	12.1	13.3
2	Atrazine	18.7	17.6	15.0	11.4	12.6	9.6	9.4	11.4
3	Benalaxyl	16.7	17.5	11.7	7.1	12.3	8.6	11.3	10.1
4	Benzoylprop-ethyl	23.1	17.6	14.8	7.7	14.0	7.7	11.7	11.2
5	Diphenamid	13.5	15.1	12.6	9.2	12.0	8.4	16.4	10.5
6	Isoprothiolane	17.6	[illegible]	10.9	[illegible]	12.9	[illegible]	[illegible]	9.5
7	Kresoxim-methyl	21.3	18.0	10.5	9.8	13.9	10.1	16.9	10.0
8	Methoprotryne	15.1	[illegible]	10.1	[illegible]	12.9	[illegible]	12.8	12.0
9	Metolachlor	17.8	17.5	10.5	11.4	13.2	8.7	14.1	10.8
10	Orbencarb	19.4	17.7	14.7	12.0	12.0	9.0	11.8	14.4
11	Penconazole	18.0	19.7	8.6	9.7	11.2	9.2	13.0	10.6
12	Picoxystrobin	19.9	18.6	10.7	8.4	12.4	9.9	13.5	11.3
13	Pirimicarb	12.0	14.2	12.3	7.2	15.7	10.7	9.6	12.6
14	Quinalphos	17.9	15.9	12.0	9.7	10.4	9.2	13.3	10.2
15	Simeconazole	17.7	23.9	8.5	12.6	13.6	8.1	18.6	11.9
16	Tebufenpyrad	21.2	16.5	11.6	11.2	12.7	10.3	12.7	10.4
17	Terbuthylazine	21.0	19.1	10.5	12.7	11.8	10.0	10.7	12.1
18	Tetraconazole	18.2	20.3	11.2	10.1	13.6	6.6	11.8	12.7
19	Thiazopyr	18.3	16.4	12.7	14.7	17.0	8.6	10.1	10.3
20	Acetochlor	17.2	16.6	15.0	18.5	14.6	10.0	12.8	12.6

The top 20 pesticide in stability were selected according to the degradation curves of 90 pesticides.

5.10 Target pesticides for “Shrunken” AOAC collaborative study protocol

To sum up, 40 pesticides have been finally selected out of the 765 pesticides with the table shown below (11 pesticides of them are co-pesticides), and GC-Q-TOF/MS and LC-Q-TOF/MS are applied to measure 20 pesticides, respectively; the Fig shows the raw data collected from this study and the relative reports compilations.

Experiment data record (765 to 40 pesticides)

No.	LC-QTOF-MS		GC-QTOF-MS	
	Name	CAS No.	Name	CAS No.
1	Acetochlor	34256-82-1	Ametryn	834-12-8
2	Ametryn	834-12-8	Atrazine	1912-24-9
3	Benalaxyl	71626-11-4	Benalaxyl	71626-11-4
4	Diphenamid	957-51-7	Benzoylprop-ethyl	22212-55-1
5	Esprocarb	85785-20-2	Acetochlor	34256-82-1
6	Fenothiocarb	62850-32-2	Diphenamid	957-51-7
7	Mepanipyrim	110235-47-7	Isoprothiolane	50512-35-1
8	Metalaxyl	57837-19-1	Kresoxim-methyl	143390-89-0
9	Methoprotryne	841-06-5	Methoprotryne	841-06-5
10	Metolachlor	51218-45-2	Metolachlor	51218-45-2
11	Orbencarb	34622-58-7	Orbencarb	34622-58-7
12	Pentanochlor	2307-68-8	Penconazole	66246-88-6
13	Picoxystrobin	117428-22-5	Picoxystrobin	117428-22-5
14	Pirimiphos-methyl	29232-93-7	Pirimicarb	23103-98-2
15	Propisochlor	86763-47-5	Quinalphos	13593-03-8
16	Quinalphos	13593-03-8	Simeconazole	149508-90-7
17	Sebuthylazine	7286-69-3	Tebufenpyrad	119168-77-3
18	Simeton	673-04-1	Terbuthylazine	5915-41-3
19	Terbuthylazine	5915-41-3	Tetraconazole	112281-77-3
20	Tetraconazole	112281-77-3	Thiazopyr	117718-60-2

LC-Q-TOFMS 20 pesticides

GC-Q-TOFMS 20 pesticides

5.11 LOQ, Linear range (R^2) of 40 Pesticides Determined by GC/LC-Q-TOF/MS

(1) LOQ, Linear range (R^2) of 20 Pesticides Determined by LC-Q-TOF/MS

No.	Name	CAS No.	Apple			Grape			Cabbage			Tomato		
			LOQ	Linear range	R^2	LOQ	Linear range	R^2	LOQ	Linear range	R^2	LOQ	Linear range	R^2
1	Acetochlor	34256-82-1	1	1~200	0.9875	5	5~200	0.9990	1	1~200	0.9908	1	1~200	0.9952
2	Ametryn	834-12-8	1	1~100	0.9893	1	1~200	0.9895	1	1~50	0.9913	1	1~50	0.9857
3	Benalaxyl	71626-11-4	1	1~100	0.9973	1	1~200	0.9987	10	10~200	0.9972	1	1~200	0.9972
4	Diphenamid	957-51-7	1	1~100	0.9965	1	1~200	0.9825	1	1~50	0.9873	1	1~200	0.9816
5	Esprocarb	85785-20-2	1	1~100	0.9976	1	1~200	0.9967	1	1~200	0.9923	1	1~200	0.9982
6	Fenothiocarb	62850-32-2	1	1~200	0.9895	1	1~200	0.9921	1	1~50	0.9931	1	1~200	0.9941
7	Mepanipyrim	110235-47-7	1	1~100	0.9965	1	1~200	0.9982	2	2~200	0.9931	2	2~200	0.9989
8	Metalaxyl	57837-19-1	1	1~200	0.9866	2	2~200	0.9818	1	1~50	0.9819	1	1~100	0.9813
9	Methoprotryne	841-06-5	1	1~200	0.9970	1	1~200	0.9974	1	1~200	0.9968	1	1~200	0.9996
10	Metolachlor	51218-45-2	1	1~200	0.9955	1	1~200	0.9967	1	1~200	0.9985	1	1~200	0.9999
11	Orbencarb	34622-58-7	1	1~100	0.9855	5	5~200	0.9989	2	2~200	0.9915	1	1~200	0.9979
12	Pentanochlor	2307-68-8	10	10~100	0.9938	2	2~200	0.9941	1	1~50	0.9955	2	2~200	0.9852
13	Picoxystrobin	117428-22-5	1	1~200	0.9902	1	1~200	0.9931	1	1~100	0.9878	1	1~200	0.9939
14	Pirimiphos-methyl	29232-93-7	1	1~100	0.9983	1	1~200	0.9985	1	1~200	0.9948	1	1~200	0.9968
15	Propisochlor	86763-47-5	10	10~200	0.9966	2	2~200	0.9952	2	2~200	0.9918	5	5~200	0.9992
16	Quinalphos	13593-03-8	1	1~200	0.9977	1	1~200	0.9852	1	1~100	0.9805	1	1~200	0.9993
17	Sebuthylazine	7286-69-3	1	1~200	0.9895	1	1~200	0.9914	1	1~50	0.9960	1	1~200	0.9930
18	Simeton	673-04-1	1	1~200	0.9805	5	5~200	0.9851	1	1~50	0.9904	5	5~100	0.9811
19	Terbuthylazine	5915-41-3	2	2~200	0.9870	1	1~200	0.9976	1	1~200	0.9963	1	1~200	0.9994
20	Tetraconazole	112281-77-3	1	1~100	0.9965	1	1~200	0.9975	r<0.99		0.9447	1	1~200	0.9997

5.11 LOQ, Linear range (R^2) of 40 Pesticides Determined by GC/LC-Q-TOF/MS

(2) LOQ, Linear range (R^2) of 20 Pesticides Determined by GC-Q-TOF/MS

No.	Name	CAS No.	Apple			Grape			Cabbage			Tomato		
			LOQ	Linear range	R^2	LOQ	Linear range	R^2	LOQ	Linear range	R^2	LOQ	Linear range	R^2
1	Acetochlor	34256-82-1	5	5~200	0.9845	10	10~200	0.9969	5	5~200	0.9987	1	1~200	0.9906
2	Ametryn	834-12-8	1	1~200	0.9820	1	1~200	0.9957	1	1~200	0.9970	1	1~100	0.9962
3	Atrazine	1912-24-9	1	1~200	0.9825	2	2~200	0.9877	1	1~200	0.9933	1	1~100	0.9928
4	Benalaxyl	71626-11-4	1	1~200	0.9856	2	2~200	0.9984	2	2~200	0.9987	5	5~200	0.9992
5	Benzoylprop-ethyl	22212-55-1	2	2~200	0.9871	5	5~100	0.9977	1	1~100	0.9969	5	5~200	0.9900
6	Diphenamid	957-51-7	1	1~200	0.9942	2	2~200	0.9880	1	1~200	0.9955	2	2~200	0.9981
7	Isoprothiolane	50512-35-1	1	1~200	0.9843	1	1~200	0.9971	1	1~200	0.9993	1	1~200	0.9997
8	Kresoxim-methyl	143390-89-0	1	1~50	0.9951	2	2~50	0.9957	1	1~200	0.9862	2	2~200	0.9859
9	Methoprotryne	841-06-5	1	1~200	0.9812	1	1~200	0.9944	1	1~200	0.9955	1	1~100	0.9938
10	Metolachlor	51218-45-2	1	1~200	0.9953	2	2~200	0.9989	5	5~200	0.9979	5	5~200	0.9946
11	Orbencarb	34622-58-7	1	1~200	0.9861	1	1~200	0.9936	1	1~200	0.9964	2	2~100	0.9932
12	Penconazole	66246-88-6	1	1~200	0.9869	1	1~200	0.9968	1	1~200	0.9971	1	1~100	0.9926
13	Picoxystrobin	117428-22-5	1	1~100	0.9899	1	1~200	0.9933	2	2~200	0.9920	1	1~200	0.9814
14	Pirimicarb	23103-98-2	1	1~200	0.9957	1	1~200	0.9931	1	1~200	0.9965	1	1~50	0.9958
15	Quinalphos	13593-03-8	5	5~50	0.9972	2	2~50	0.9994	2	2~200	0.9850	1	1~100	0.9891
16	Simeconazole	149508-90-7	1	1~200	0.9933	2	2~200	0.9995	1	1~200	0.9984	2	2~200	0.9953
17	Tebufenpyrad	119168-77-3	1	1~200	0.9832	1	1~200	0.9950	1	1~200	0.9983	1	1~50	0.9970
18	Terbuthylazine	5915-41-3	1	1~200	0.9855	1	1~200	0.9968	1	1~200	0.9976	1	1~100	0.9959
19	Tetraconazole	112281-77-3	1	1~200	0.9899	1	1~200	0.9945	1	1~200	0.9967	1	1~100	0.9994
20	Thiazopyr	117718-60-2	1	1~200	0.9996	5	5~200	0.9989	10	10~200	0.9923	2	2~200	0.9994

5.12 40 pesticide categories detected by GC/LC-QTOF/MS

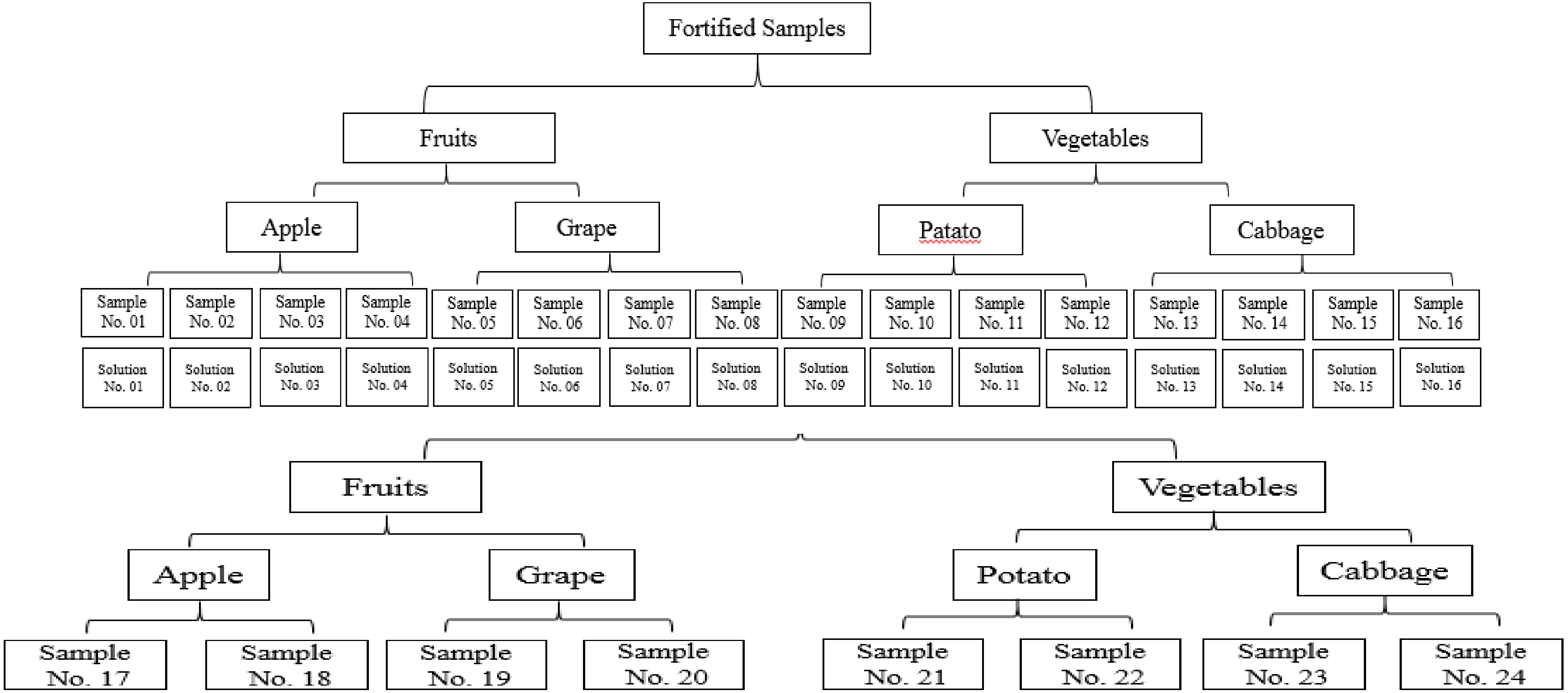
20 pesticide categories detected by GC-QTOF/MS

classified per chemical compositions		classified per functions	
Carbamate	1	Herbicide	**10**
Organophosphorus	1	Insecticide	**3**
Organohalogen	4	fungicide	**7**
Organic sulfu	1		
Organonitrogen	11		
Other	**2**		

20 pesticide categories detected by LC-QTOF/MS

classified per chemical compositions		classified per functions	
Carbamate	2	Herbicide	**12**
Organophosphorus	2	Insecticide	**3**
Organonitrogen	12	fungicide	**5**
Organohalogen	3		
Other	**1**		

6.1 Fortified and Pesticide Aged Samples for the Collaborative study



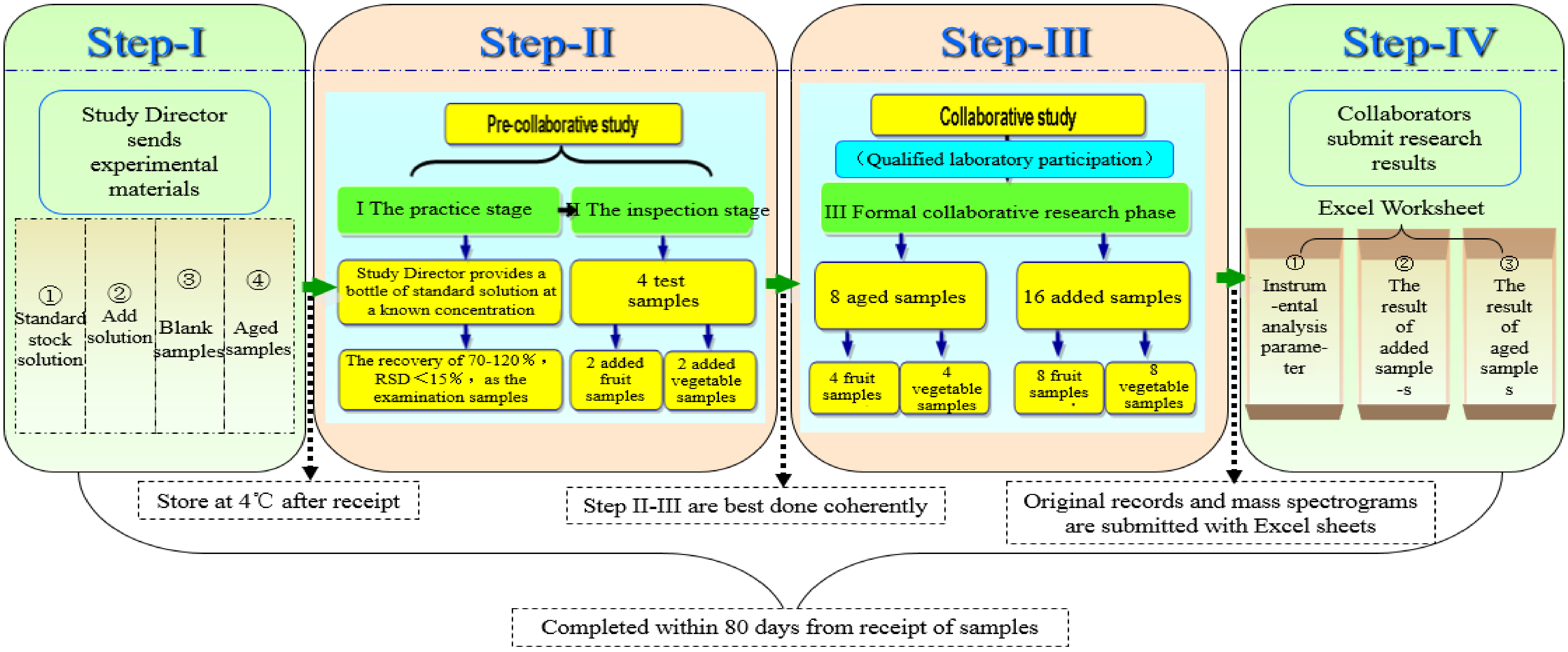
Number of Fortified and Pesticide Aged Samples for the Collaborative study

6.2 Collaborative study sample quantity and concentration levles of target pesticides

- Each participating lab is to determine a total of 24 collaborative samples (16 foritified samples and 8 aged samples).
- Each sample is only enough for one experiment, which is to say that each lab has only one experiment opportunity for each sample and must ensure success at one stroke.
- Therefore, Study Director reiterates here that every lab must treat this study with utmost care and conscientiousness.

"one sample good only for one shot"
the pre-study played a vital role in the study

6.3 AOAC collaborative study process



6.4 AOAC collaborative study outlook

- **We will invite over 30 laboratories from 15 countries and regions in the five continents to participate in the study.**
- **Agilent company has given tremendous support for this collaborative study, so it is also our partner in co-sponsoring this study program. Here, we thank Agilent for its big support.**
- **We sincerely welcome friends who are interested in this technology to participate actively!**

6.5 Protocol & Method（see attachments）

- AOAC collaborative study protocol
- AOAC collaborative study method

Join Us

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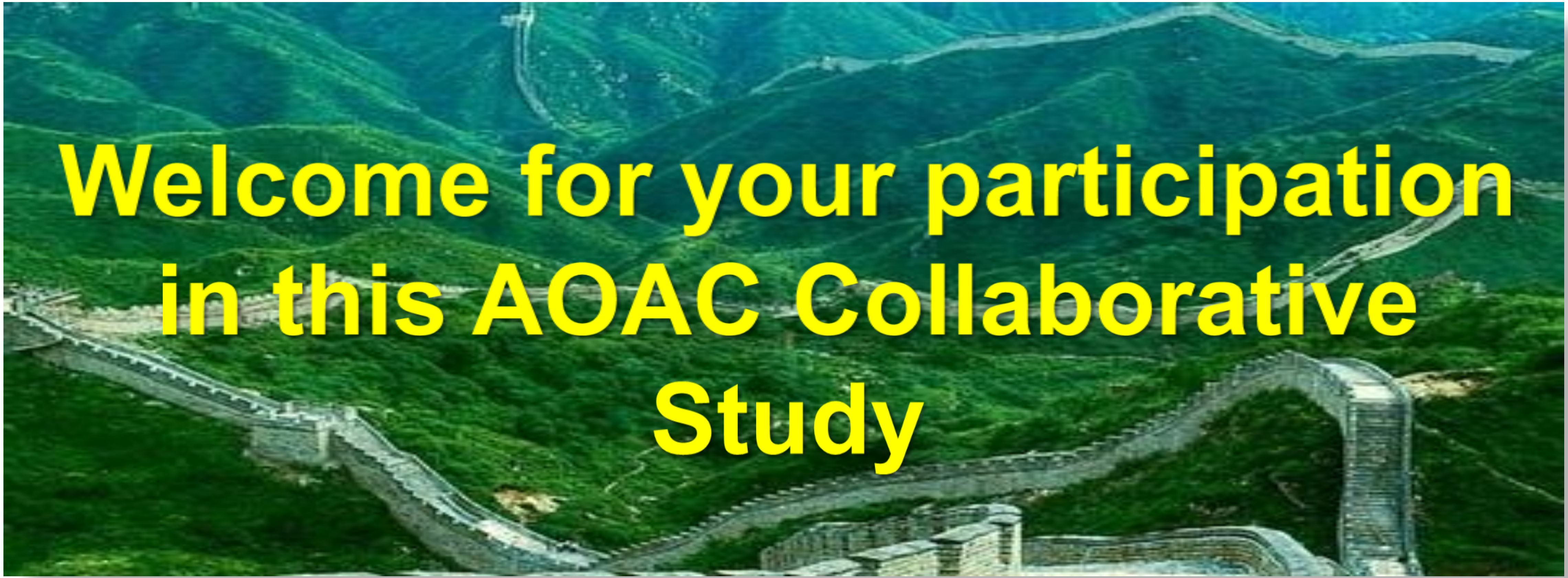

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