

ION CHROMATOGRAPHY APPLICATION NOTES

Pesticides



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Application of ion chromatography in pesticide industry

Pesticides refer to a class of drugs used to kill insects, sterilize and kill harmful animals (or weeds) in order to ensure and promote the growth of plants and crops in agricultural production, especially those used in agriculture to prevent and control diseases and insect pests and regulate plant growth and weeding. It is widely used in agriculture, forestry and animal husbandry production, environmental and household hygiene, pest control and epidemic prevention, mold and moth prevention of industrial products, etc. There are many kinds of pesticides, which can be divided into insecticides, acaricides, rodenticides, nematocides, molluscicides, fungicides, herbicides, plant growth regulators, etc; According to the source of raw materials, it can be divided into mineral pesticides (inorganic pesticides), biological pesticides (NATURAL organics, microorganisms, antibiotics, etc.) and chemical synthetic pesticides; According to the chemical structure, they mainly include organochlorine, organophosphorus, organic nitrogen, organic sulfur, carbamate, pyrethroid, amide compounds, ether compounds, phenolic compounds, phenoxy-carboxylic acids, amidines, triazoles, heterocycles, benzoic acids, etc. they are organic synthetic pesticides. Most pesticides have complex structures and various varieties. Although most of them can be analyzed by HPLC or GC, ion chromatography is a better choice for some compounds that do not have optical absorption and can be ionized.

Ion chromatography was initially mainly used to analyze inorganic anions and anions. With the development of ion chromatography technology, its application scope has gradually expanded. With the strengthening of people's awareness of health and environmental protection, IC has developed rapidly in the detection of pesticides, and many simple and practical detection methods have been established. This scheme mainly introduces some applications of ion chromatography in pesticide detection for your reference.

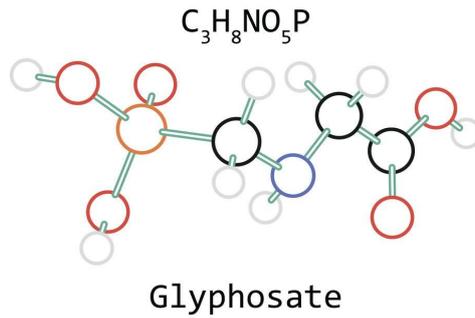
1. Application of ion chromatography in pesticide principal components and impurities

1.1 Determination of glyphosate in pesticides



Glyphosate is chemically known as N - (phosphonic acid methyl) glycine, also known as glyphosate, Nongda, etc. it is an amino acid derivative. It is a very stable compound with a solubility of 1.2% in water and insoluble in general organic reagents. Glyphosate is a broad-chromatogram herbicide with the advantages of low toxicity and high efficiency. However, glyphosate is not easy to degrade in the environment and will pollute the environment. Due to the weak absorption of glyphosate to light, derivatization or low wavelength UV absorption is required for HPLC separation. The detection time is long and the sensitivity is not high. Glyphosate has large ionization in water, so it is suitable for the detection of ion chromatography conductivity method.

1.1.1 Determination of glyphosate (hydroxyl system) in pesticides by Ion Chromatography



- Analytical Column: SH-G-1+SH-AC-11
- Mobile Phase: 30 mM KOH (EG)
- Flow Rate: 1.0 mL/min
- Column Temperature: 35°C
- Suppressor: SHY-A-6
- Injection Volume: 50 μL
- Detector: Conductivity Detector

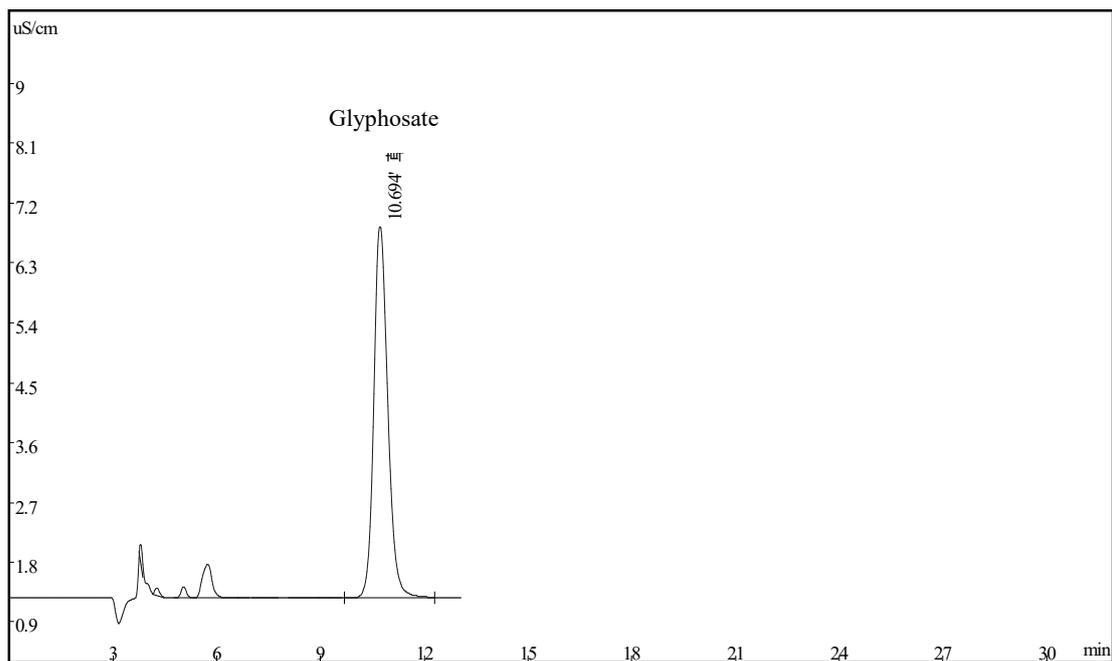
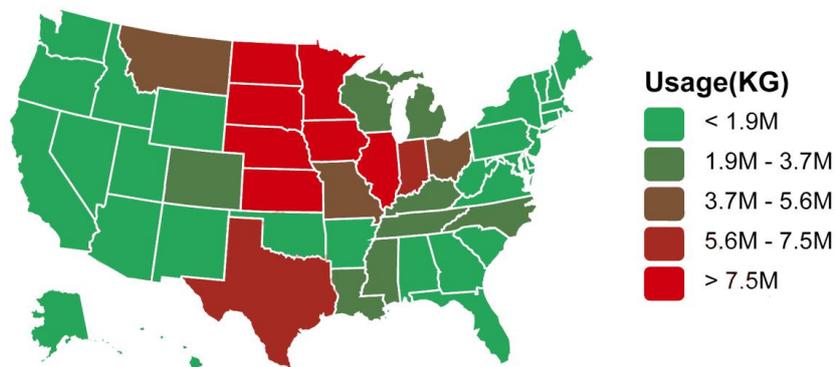


Fig. 1 chromatogram of glyphosate standard

1.1.2 Determination of glyphosate (carbonate system) in pesticides by Ion Chromatography

Here's how much glyphosate has been used in your state!



- Analytical Column: SH-G-1+SH-AC-12C
- Mobile Phase: 7.0 mmol/L Na₂CO₃+6.0 mmol/L NaHCO₃
- Flow Rate: 0.7 mL/min
- Column Temperature: 35°C
- Suppressor: SHY-A-6
- Injection Volume: 50 μL
- Detector: Conductivity Detector

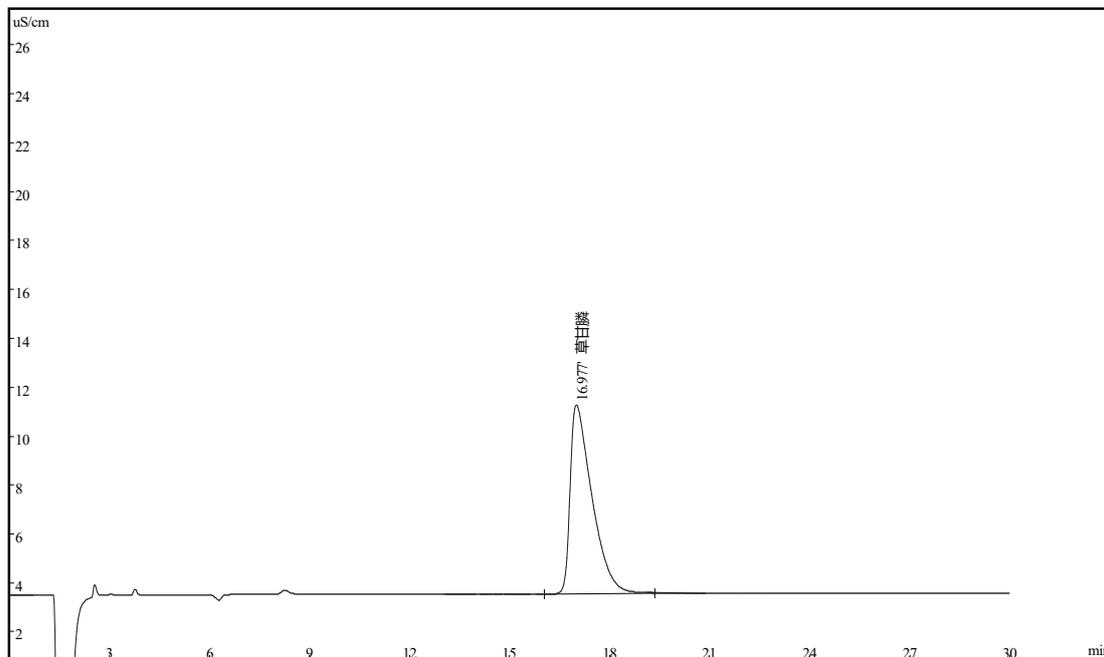


Fig. 2 chromatogram of glyphosate standard

1.2 Determination of methyl sulfonic acid (MSA) in chlormethoxam granules

Thiamethoxam is an efficient and broad-chromatogram insecticide, which has a good control effect on Lepidoptera, Hemiptera, Hymenoptera, Coleoptera and so on. Thiamethoxam is a new type of saline alkali insecticide with high efficiency, safety and selectivity, which is more and more widely used in agricultural production.

- Analytical Column: SH-G-1+SH-AP-4
- Mobile Phase: KOH Gradient
 - 0-10min, 6mmol/L;
 - 10.1-30min, 60mmol/L;
 - 30.1-35min, 6mmol/L
- Flow Rate: 1.0 mL/min
- Suppressor: SHY-A-6
- Injection Volume: 25 μ L
- Pretreatment: weigh about 1 g of sample (accurately record the mass to 0.0001 g), dilute the sample solution moderately, and pass 0.22 μ M filter membrane injection analysis.

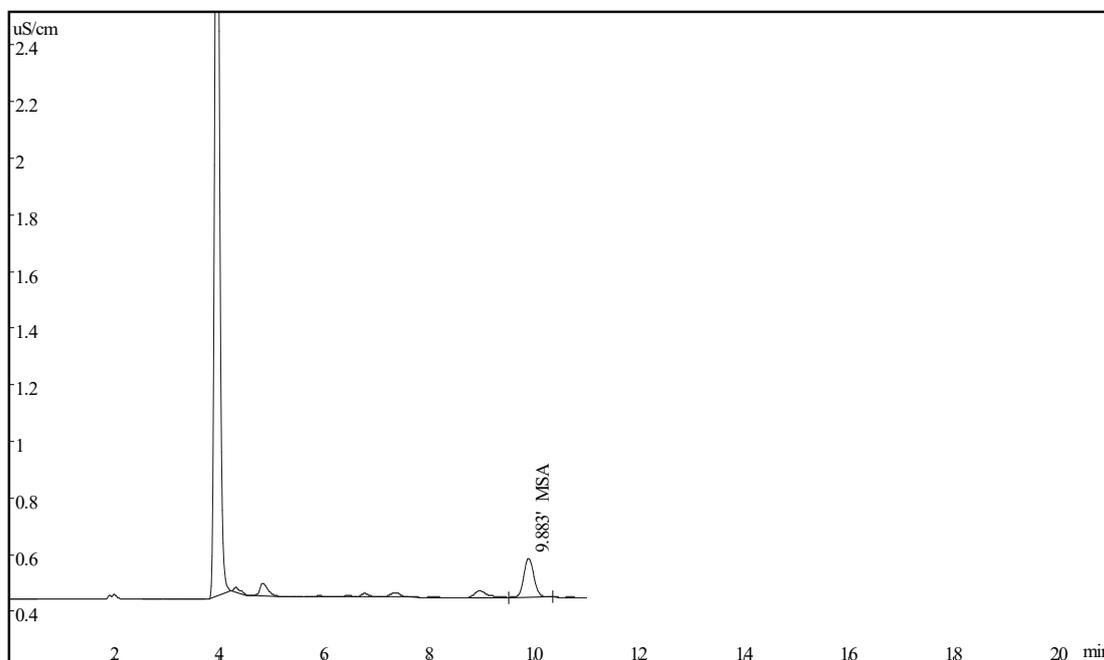


Fig. 1 analysis chromatogram of MSA in chlormethoxam granules

1.3 Determination of aluminum triethylphosphonate in ethylaluminum manganese zinc

Ethylaluminum manganese zinc is a mixture of aluminum triethylphosphonate and mancozeb, which has obvious synergistic effect on Downy Mildew and Phytophthora. Aluminum triethylphosphonate is an endophytic bactericidal component, which can conduct up and down in plants. It has protective and therapeutic effects; Mancozeb is a protective bactericidal component, which is mainly sterilized by metal ions. Its bactericidal mechanism is to inhibit the oxidation of pyruvate in the metabolic process of bacteria, resulting in the death of bacteria. The inhibitory process has six action sites, so the bacteria polar pheasant has drug resistance. The two are mixed, complementary and synergistic, with a wider range of disease prevention.

- Analytical Column: SH-G-1+SH-AC-4
- Mobile Phase: 2.4 mM Na₂CO₃+6.0 mM NaHCO₃
- Flow Rate: 1.2 mL/min
- Column Temperature: 35°C
- Suppressor: SHY-A-6
- Injection Volume: 25 μL
- Pretreatment: weigh about 0.2 g of sample (accurately record the mass to 0.0001 g) into a 100 ml volumetric flask, add 20 ml of ultrapure water for ultrasonic treatment for 30 min, and shake the eluent to volume. Take 1 ml of sample solution into a 100 ml volumetric flask, shake the eluent to a constant volume and pass it through 0.22 μ M filter membrane injection analysis.

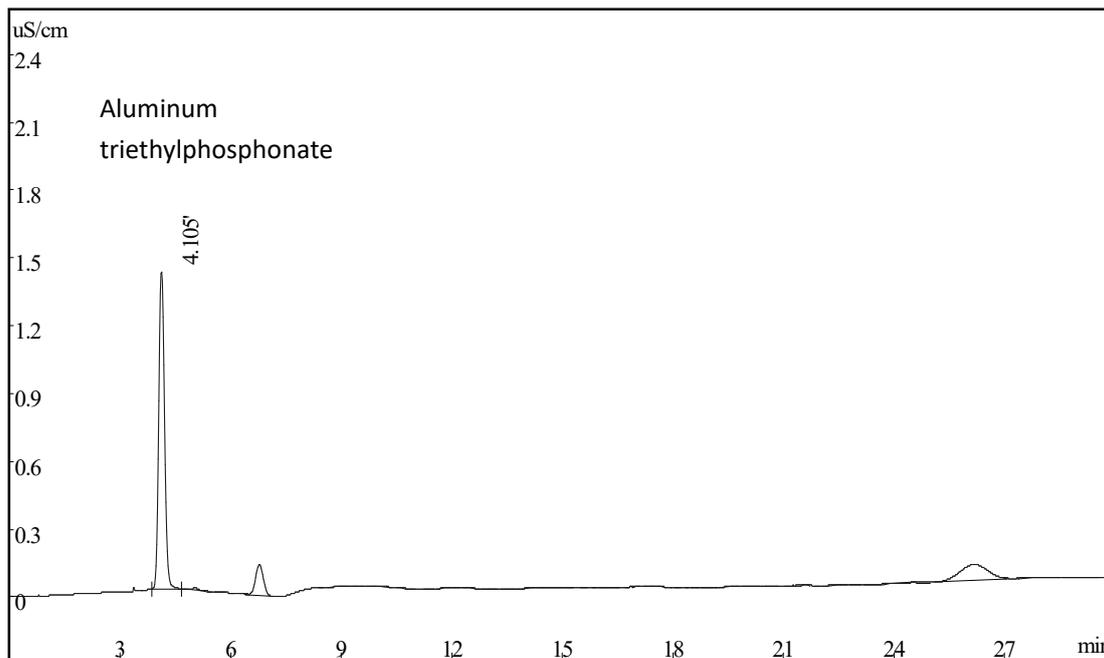


Fig. 1 analysis chromatogram of aluminum triethylphosphonate in ethylaluminum manganese zinc

1.4 Determination of chloride ion in kasugamycin



kasugamycin is also known as Jiashou rice, kasugamycin, kesmin, etc. It is a metabolite of microorganisms and belongs to agricultural broad-chromatogram bactericide with strong permeability and internal absorption. kasugamycin has good control effect on a variety of fungal diseases. kasugamycin has good control effect on rice blast, but also has a good control effect on other diseases, such as citrus

sandskin disease, pepper bacterial scab, celery early blight and so on. Kasugamycin can be used in most crops (except beans, fir and lotus root). kasugamycin is listed as the recommended pesticide for the production of pollution-free agricultural products by the Ministry of agriculture because of its low residue and pollution-free. The detection of chloride ion has important guiding significance for the production of kasugamycin.

- Analytical Column: SH-G-1+SH-AC-4
- Mobile Phase: 2.4 mM Na₂CO₃+6.0 mM NaHCO₃
- Flow Rate: 1.2 mL/min
- Column Temperature: 35°C
- Suppressor: SHY-A-6
- Injection Volume: 25 μL
- Pretreatment: weigh about 0.1 g of sample (accurately record the mass to 0.0001 g) into a 100 ml volumetric flask, add ultrapure water to the scale, shake well and pass 0.22 μ M filter membrane injection analysis.

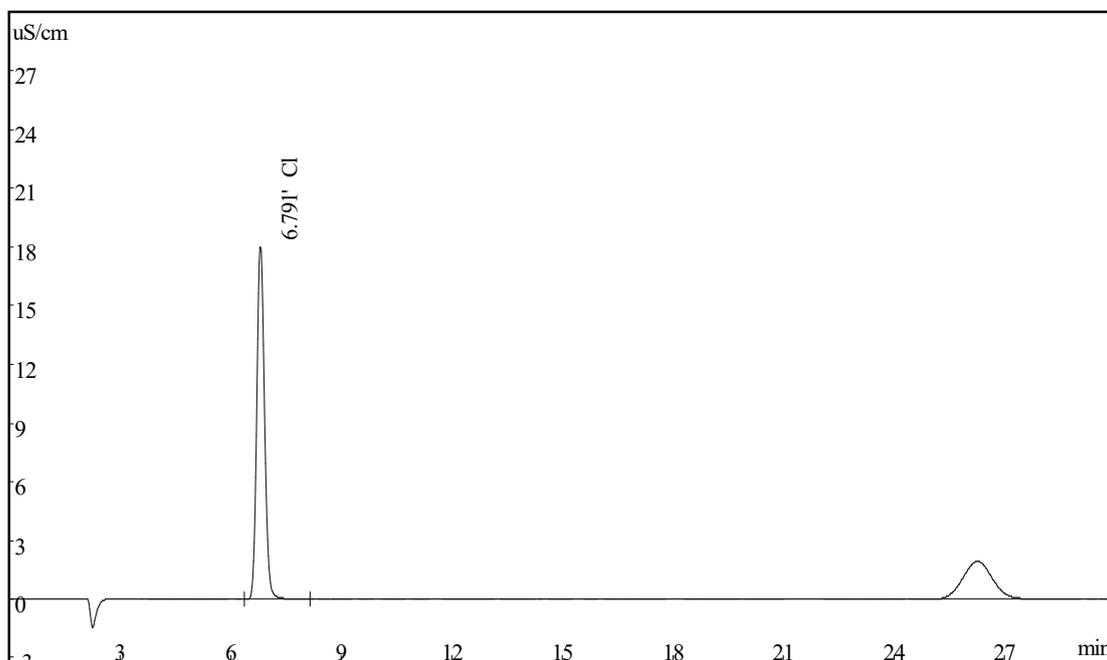


Fig. 1 analysis chromatogram of chloride ion in kasugamycin

1.5 Determination of sodium ion, N-methylpiperidine and

methylpiperidium in methylpiperidium

Methylpiperonium, also known as N · N-dimethylpiperidine, ketamine, is a new plant growth regulator, which has a good internal absorption and conduction effect on plants. It can promote the reproductive growth of plants; Inhibit the vigorous growth of stems and leaves, control lateral branches, shape the ideal plant type, improve the number and vitality of roots, increase the weight and quality of fruits. Widely used in cotton, wheat, rice, peanuts, corn, potatoes, grapes, vegetables, beans, flowers and other crops. Marking the mass concentration of the active ingredient in the pesticide dosage form is of great significance for consumers to buy and use the product. In addition, it is also important to detect the content of impurities in the pesticide dosage form. N-methylpiperidine is an important intermediate for the synthesis of meperidonium, which has a similar structure to meperidonium.

- Analytical Column: SH-G-1+SH-CC-4
- Mobile Phase: 9.5 mM Methyl sulfonic acid
- Flow Rate: 1.0 mL/min
- Column Temperature: 35°C
- Suppressor: SHY-C-5
- Injection Volume: 25 μL
- Pretreatment: weigh about 1 g of sample (accurately record the mass to 0.0001 g) into a 100 ml volumetric flask, add ultrapure water to the scale, shake well and pass 0.22 μ M filter membrane injection analysis.

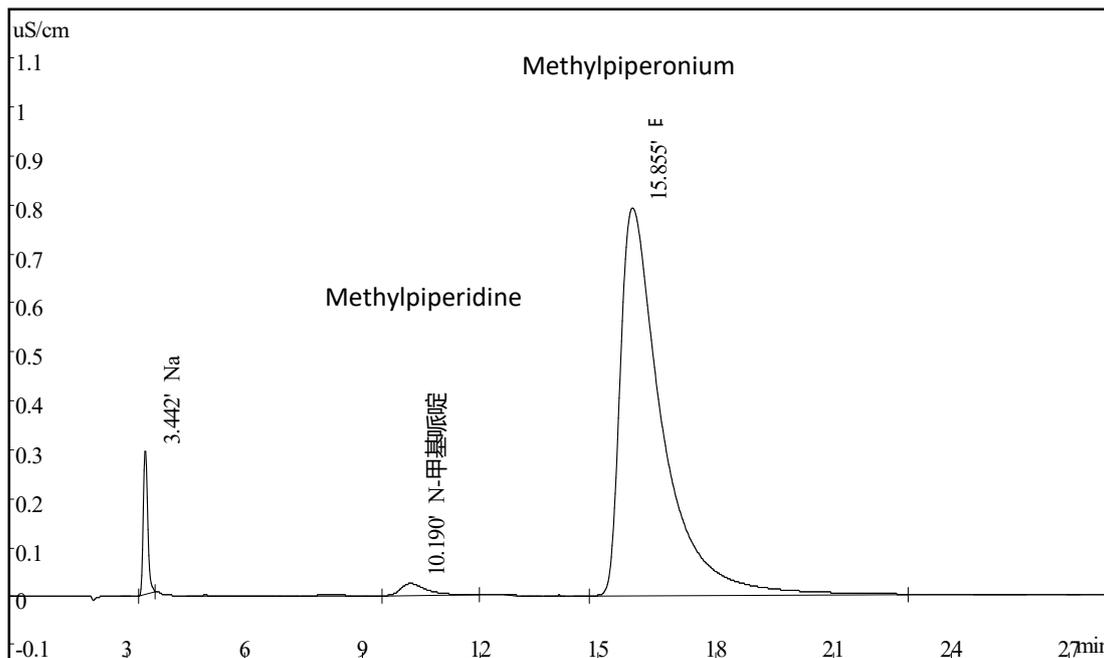
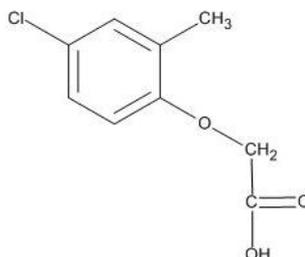


Fig. 1 analysis chromatogram of mepinum sample

1.6 Determination of dimethylamine in dimethyltetra chloride salt



Dimethyltetrachloride (2,4-D) is a phenoxyacetic acid selective herbicide with strong internal absorption conductivity. It is mainly used for stem and leaf treatment after seedling. It is used to control broad-leaved weeds of rice, corn, wheat and other crops, especially dayflower and morning glory, which are difficult to be controlled by Nongda. The action mechanism of the agent is to pass through the cuticle and cell plasma membrane, inhibit nucleic acid metabolism and protein synthesis at the top of the plant, stop the growth of the growth point, and the young leaves cannot stretch; The medicament transmitted to the lower part of the plant increases the synthesis of nucleic acid and protein in plant stem tissue, promotes abnormal cell division, expands the root tip, loses the ability to absorb nutrients, and

finally leads to plant death.

At present, the common dimethyl tetrachloride salts in China include 2,4-D sodium salt, potassium salt, ammonium salt, dimethylamine salt, etc. among them, 2,4-D dimethylamine salt has many advantages over other salts, such as wider applicable temperature, higher activity, stable efficacy, reduced impurities, etc. In order to standardize the market order and prevent bad merchants from shoddy goods, it is of great significance to detect cations in dimethyltetrachloride.

- Analytical Column: SH-G-1+SH-YS-50
- Mobile Phase: 2.0 mM Methyl sulfonic acid
- Flow Rate: 1.0 mL/min
- Suppressor: SHY-C-5
- Injection Volume: 25 μ L
- Pretreatment: take 100 μ L sample (weigh, accurately record the mass, accurate to 0.0001 g), dissolve it with ultrapure water to a constant volume of 100 ml, shake it well and pass 0.22 μ M filter membrane injection analysis.

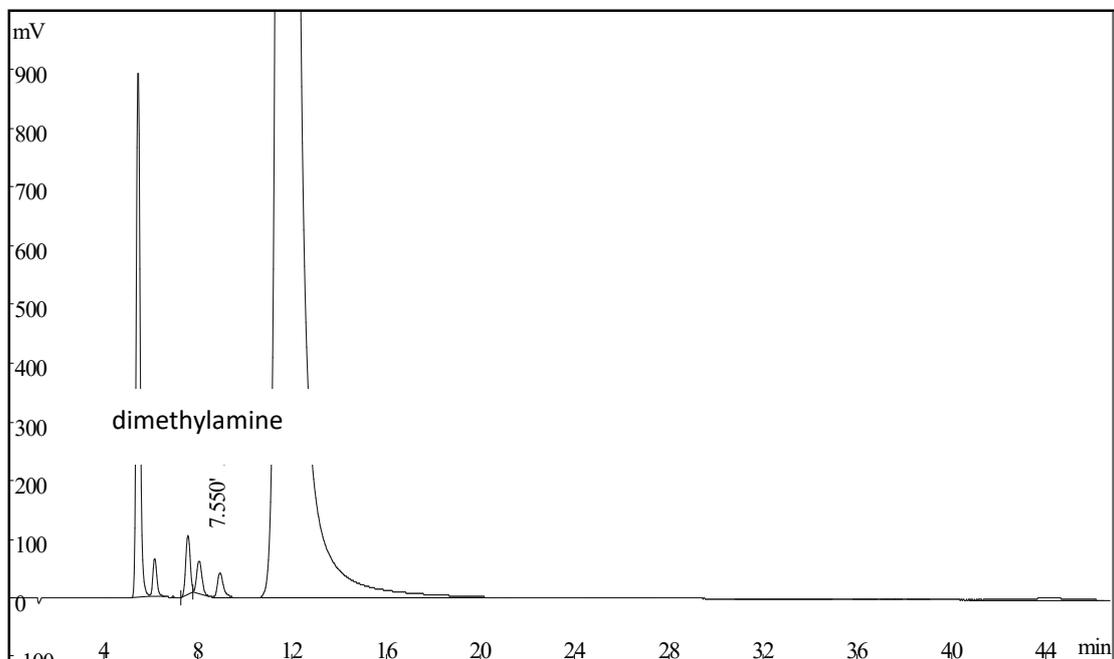


Fig. 1 chromatogram of dimethylamine in dimethyltetrachloride salt

1.7 Determination of sodium ion and ammonium radical in

Glyphosate



Glyphosate, whose scientific name is N - (o-acylmethyl) glycine, is a kind of biocidal chronic internal organophosphorus herbicide with the characteristics of high efficiency, low toxicity and broad chromatogram. Due to the low solubility of glyphosate in water, glyphosate acid is usually prepared into water-soluble salts in practical application, such as glyphosate sodium salt, potassium salt, ammonium salt, dimethylamine salt and isopropylamine salt. The mass fraction of Na⁺, K⁺, NH₄⁺, dimethylamine, isopropylamine and other cations in glyphosate samples can be quickly detected by suppressed conductivity method. This method meets the requirements of national standards GB / T 20684-2017 glyphosate water agent and GB / T 20686-2017 glyphosate soluble powder (granule).

- Analytical Column: SH-G-1+SH-CC-4
- Mobile Phase: 4.0 mM Methyl sulfonic acid
- Flow Rate: 1.0 mL/min
- Injection Volume: 25 μL
- Suppressor: SHY-C-5
- Pretreatment: measure 1 ml of glyphosate sample (weigh and accurately record the mass to 0.0001 g), dilute with ultrapure water to 100 ml, shake well and dilute 100 times, and pass 0.22 μ M filter membrane injection analysis.

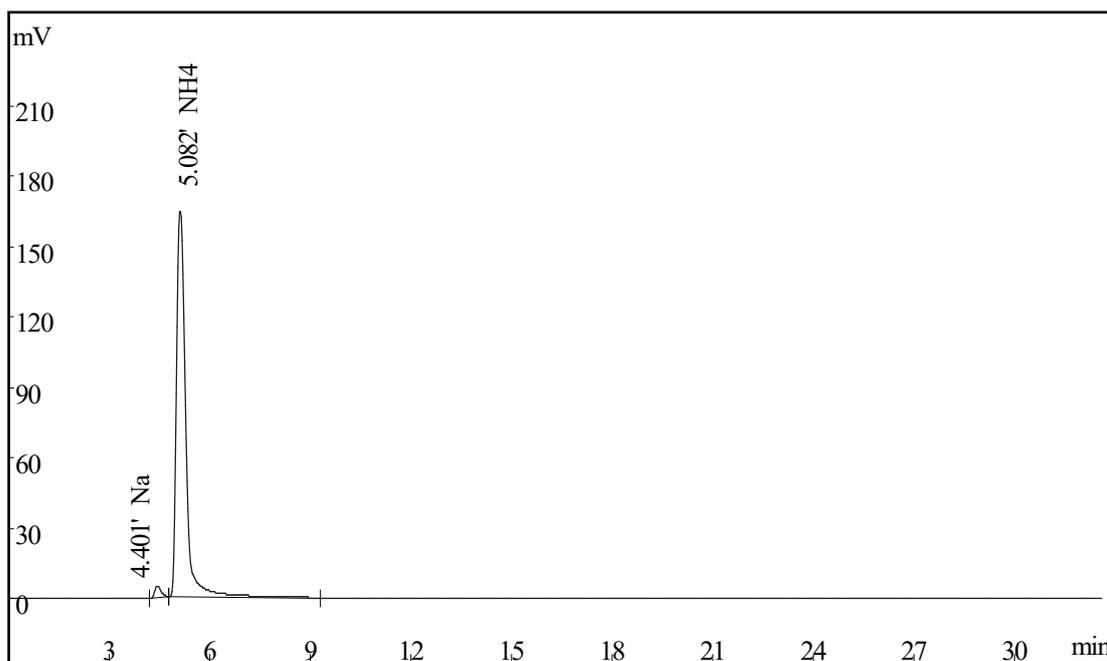


Fig. 1 chromatogram of sodium ion and ammonium radical in Glyphosate

1.8 Determination of anions in ammonium chloride



Ammonium chloride is colorless crystal or white crystalline powder, odorless, salty and cool in taste, and hygroscopic. It is divided into industrial ammonium chloride and agricultural ammonium chloride. Among them, the quality standards of industrial ammonium chloride first-class products are as follows: the appearance is white crystal; Ammonium chloride content (calculated on dry basis) > 99.3%; Water content < 0.7%; Burning residue < 0.4%; Iron content < 0.001%; Heavy metal content (calculated by Pb) < 0.0005%; Sulfate content (calculated by SO_4^{2-}) < 0.05%; The pH value is between 4.0-5.8. Agricultural ammonium chloride can be used as nitrogen fertilizer, and its action mechanism is similar to that of ammonium sulfate, but the

soil acidification caused by the application of ammonium chloride is more serious than that of ammonium sulfate. It can be used as base fertilizer and topdressing, but not as seed fertilizer. In addition, it is not allowed to apply a large amount of chlorine avoiding crops (tobacco, sugarcane, potato, etc.), in which impurity ions such as fluorine and bromine will affect the quality of ammonium chloride, so it is necessary to detect the anions.

- Analytical Column: SH-G-1+SH-AC-11
- Mobile Phase: 14.5 mM KOH (EG)
- Flow Rate: 1.0 mL/min
- Column Temperature: 35°C
- Suppressor: SHY-A-6
- Injection Volume: 25 μ L
- Pretreatment: weigh about 0.1 g of the sample (record the mass, accurate to 0.0001 g), dilute and dissolve it with ultrapure water, fix the volume to 100 ml, ultrasonic for 5 minutes, and pass 0.22 μ M filter membrane injection analysis.

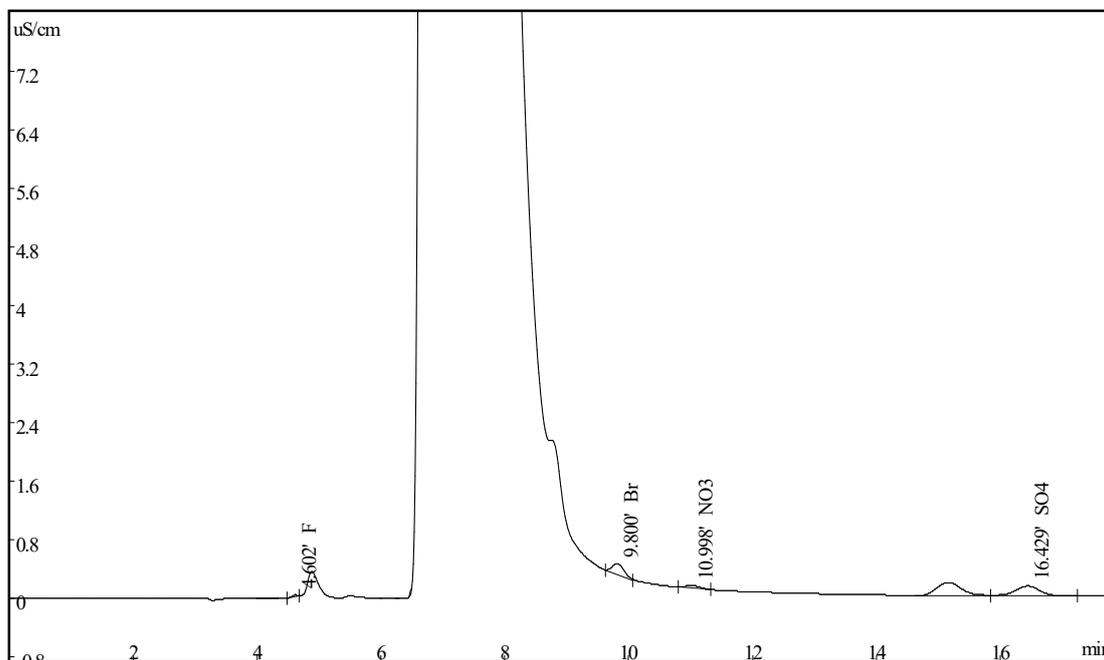


Fig. 1 anion chromatogram in ammonium chloride

1.9 Determination of chloride ion in Maleic Hydrazide



Maleic Hydrazide is also called malazide or anthocyanin. A selective herbicide and a temporary plant growth inhibitor. The pure product is white crystal. The solubility in water is 0.2% (25 °C). Its sodium, potassium, ammonium salts and organic alkali salts are easily soluble in water. Stable in nature. The dosage forms include water agent, technical drug, ethanolamine salt solution, etc. It can be used to prevent the germination of potatoes, onion, garlic and radish during storage. Among them, chloride ion, as an impurity ion, will affect the quality of Maleic Hydrazide, so it is necessary to detect the chloride ion.

- Analytical Column: SH-G-1+SH-AP-2
- Mobile Phase: 2.5 mMNaHCO₃+12% Acetonitrile
- Flow Rate: 1.0 mL/min
- Column Temperature: 35°C
- Suppressor: SHY-A-6
- Injection Volume: 25 μL

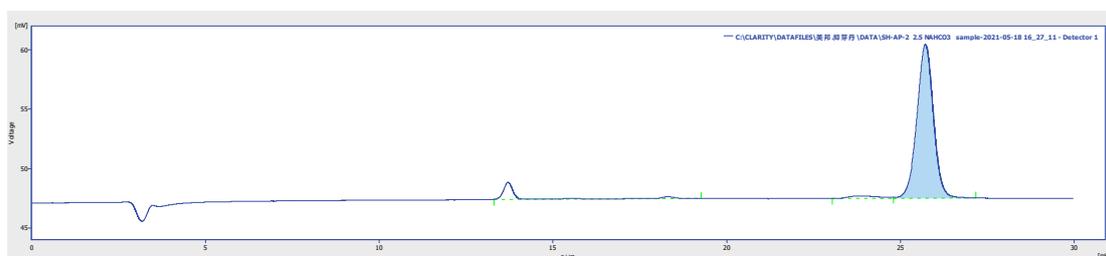
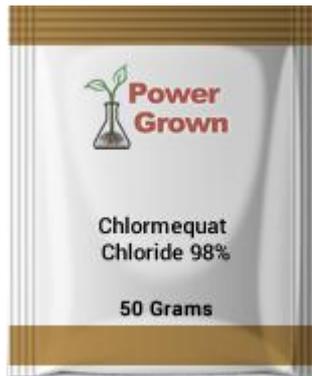


Fig. 1 chloride ion chromatogram in Maleic Hydrazide

1.10 Determination of chlormequat in pesticide chlormequat



Chlormequat (CCC) is a quaternary ammonium salt plant growth regulator. The chemical formula is $C_5H_{13}Cl_2N$. The appearance is white crystal, fishy smell and easy to deliquesce. Chlormequat is an excellent plant growth regulator, which can be used in wheat, rice, cotton, tobacco, corn, tomato and other crops. It can inhibit the elongation of crop cells, but does not inhibit cell division. It can make the plant shorter, the stem thicker and the leaf color green. It can make the crops resistant to drought and waterlogging, prevent the crops from overgrowth and lodging, resist salt and alkali, and prevent the cotton from falling the bell, It can increase the tuber of potato. Chloramphenicol is easily degraded by enzymes in soil and is not easy to be fixed by soil. Therefore, it does not affect soil microbial activities or can be decomposed by microorganisms, so it does not harm the environment. As an excellent plant growth regulator, the detection of chlormequat is of great significance for the monitoring of its production and use process.

- Analytical Column: SH-G-1+SH-CC-4
- Mobile Phase: 4.5 mM Methyl sulfonic acid
- Flow Rate: 1.0 mL/min
- Column Temperature: 35°C
- Suppressor: SHY-C-5
- Injection Volume: 25 μ L

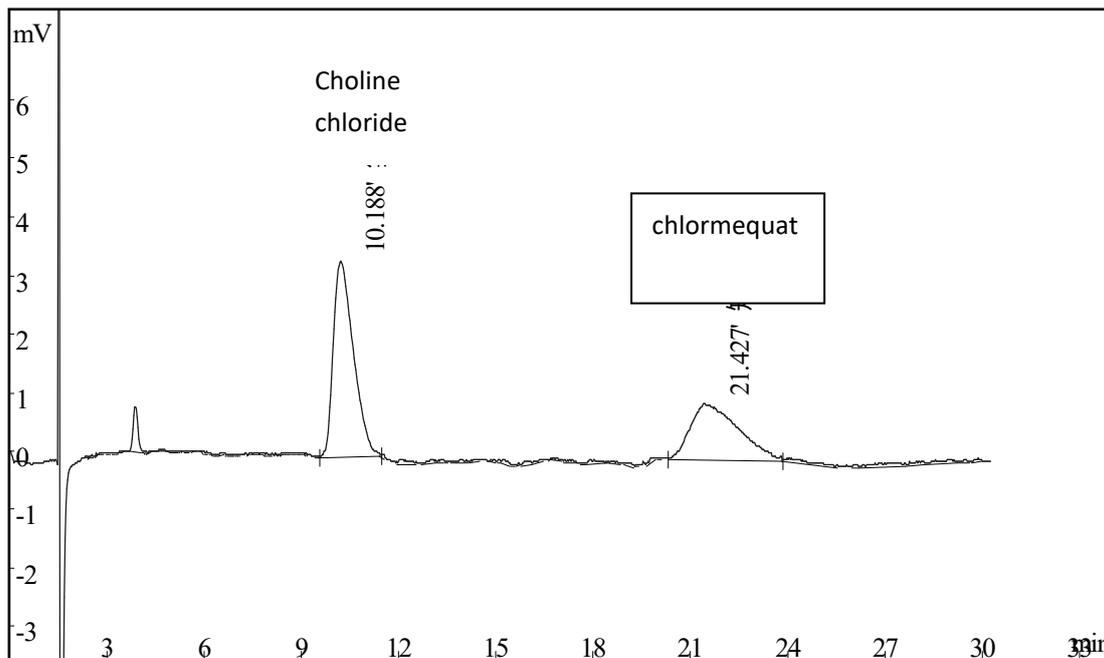


Fig. 1 chromatogram of chlormequat standard

1.11 Determination of ethephon, phosphite and phosphoric acid in pesticide Ethephon

Ethephon, a chemical formula of $C_2H_6ClO_3P$, is a high quality and efficient plant growth regulator. It has the physiological effects of enhancing hormone secretion, accelerating maturation, abscission, senescence and promoting flowering. Under certain conditions, ethephon can not only release ethylene by itself, but also induce plants to produce ethylene. At present, the main synthetic processes are accompanied by the formation of by-products phosphite and phosphoric acid in the process of reaction. Therefore, monitoring phosphite and phosphoric acid is of guiding significance to the quality of their products.

- Analytical Column: SH-G-1+SH-AC-1
- Mobile Phase: 3.6 mM Na_2CO_3 +4.5 mM $NaHCO_3$
- Flow Rate: 1.5 mL/min
- Column Temperature: 35°C
- Suppressor: SHY-A-6
- Injection Volume: 25 μ L

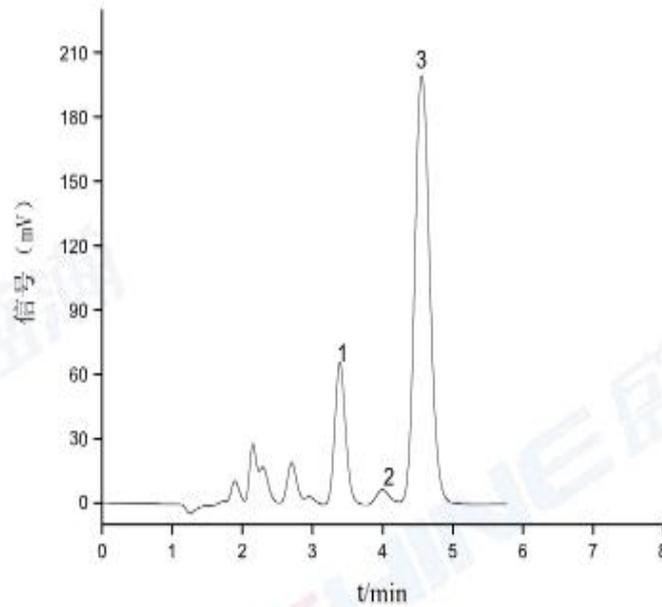


Fig. 1 Determination chromatogram of ethephon water agent (1-phosphite, 2-phosphoric acid, 3-ethephon)

1.12 Determination of chloride ion and choline chloride in pesticide choline chloride and its preparations



Choline chloride is an organic substance with the chemical formula of $C_5H_{14}ClNO$. It is white, hygroscopic crystal, tasteless, fishy and unstable in alkaline solution.. Choline chloride is a plant photosynthesis promoter, which has a significant effect on increasing yield. Spraying wheat and rice at booting stage can promote spikelet

differentiation and produce more spikelets and grains. Spraying at grain filling stage can speed up grain filling and make spikelets and grains full. It can also be used to increase the yield of corn, sugarcane, sweet potato, potato, radish, onion, cotton, tobacco, vegetables, grapes, mango, etc. the effect is stable under different climate and ecological environment conditions. As an impurity ion, chloride ion must be monitored in its production and use process. Therefore, monitoring choline chloride and chloride ion has guiding significance for the quality of its products.

Choline chloride test conditions:

- Analytical Column: SH-G-1+SH-CC-4
- Mobile Phase: 12 mM Methyl sulfonic acid
- Flow Rate: 1.0 mL/min
- Column Temperature: 35°C
- Suppressor: SHY-C-5
- Injection Volume: 25 μ L

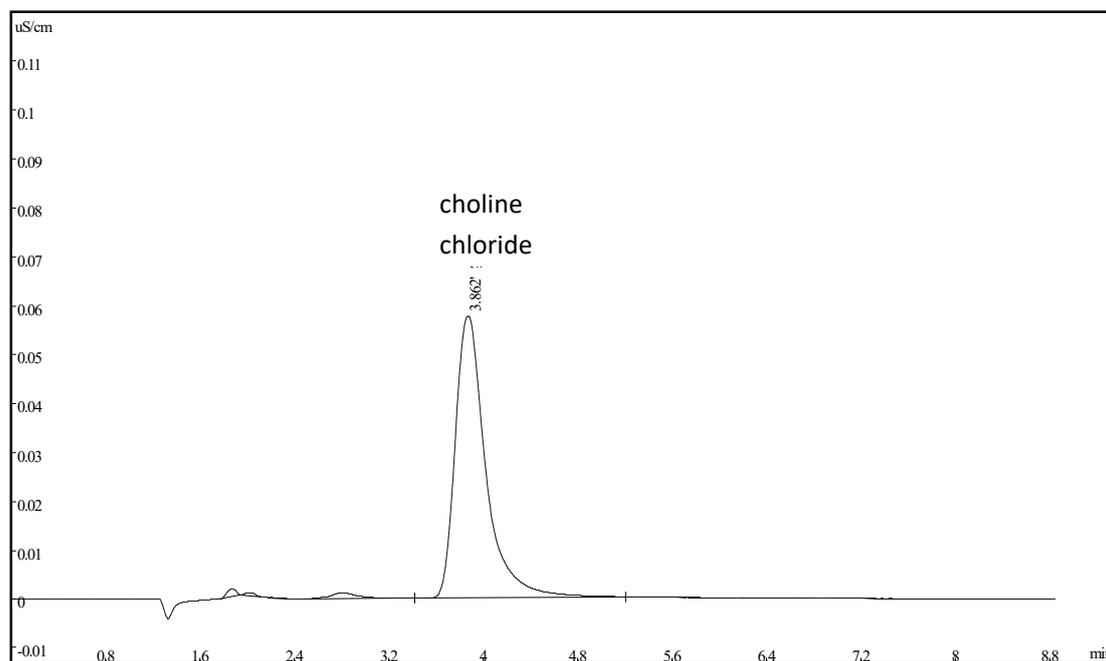


Fig. 1 chromatogram of choline chloride standard

Test conditions of chloride ion in choline chloride:

- Analytical Column: SH-G-1+SH-AP-1
- Mobile Phase: 15 mM KOH (EG)
- Flow Rate: 0.8 mL/min

- Column Temperature: 35°C
- Suppressor: SHY-A-6
- Injection Volume: 25 μL

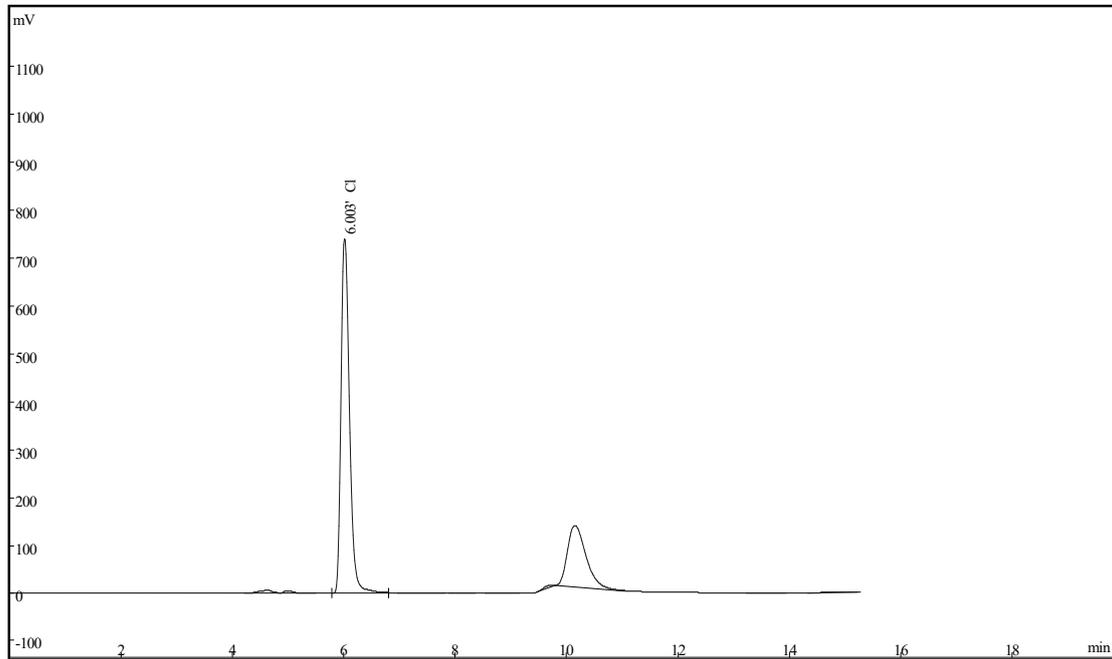


Fig. 2 chloride ion chromatogram in 5% choline chloride wettable powder

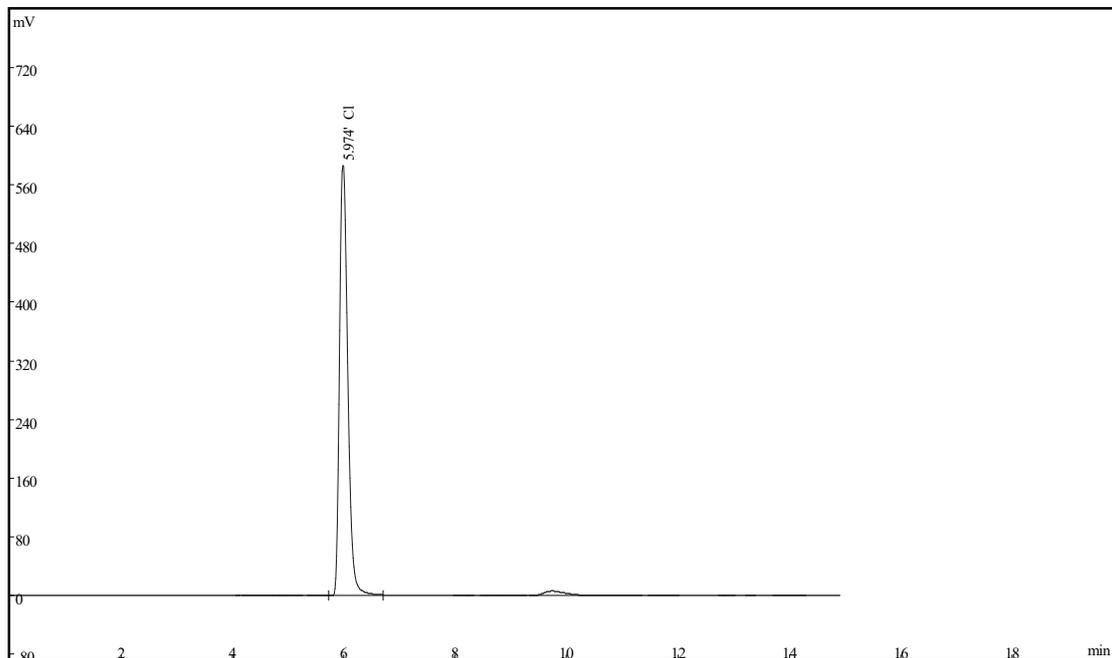


Fig. 3 chloride ion chromatogram in 20% choline chloride naphthylacetic acid water agent

2. Application of ion chromatography in combination of pesticide principal components and impurities

2.1 Determination of five organophosphines by ion chromatography tandem mass spectrometry

Organophosphine pesticides are mainly used to control plant diseases, insects and weeds and regulate plant growth, including adjuvants and synergists to improve the efficacy of pesticides. At present, the area of cultivated land in the world has decreased, the population has increased, and the food problem is prominent. Improving grain yield is inseparable from pesticides. Therefore, it is necessary to detect organophosphine pesticides. This scheme mainly detects five kinds of organophosphines: glyphosate, aminomethyl phosphate, glufosinate, ethephon, glyphosate, ¹³C glufosinate and ¹³C glyphosate.

Ion chromatography conditions:

- Analytical Column: Dionex IonPac AS19 (250mm*2mm)
- Mobile Phase: KOH Gradient
 - 0-2 min, 6mmol/L;
 - 2-20min, 6-40mmol/L;
 - 20-35min, 40mmol/L;
 - 35.1-40min, 6mmol/L
- Flow Rate: 0.35 mL/min
- Injection Volume: 100 μL

Mass chromatogram conditions:

- Atomization gas flow: 1.4 L/min
- Desolvent gas flow: 4.5 L/min
- Blowback flow: 1.5 L/min
- Desolvent gas temperature: 480°C
- Collision gas flow: 0.40 mL/min
- Capillary high pressure: 4.2kV

The internal standard method was used to test the standard

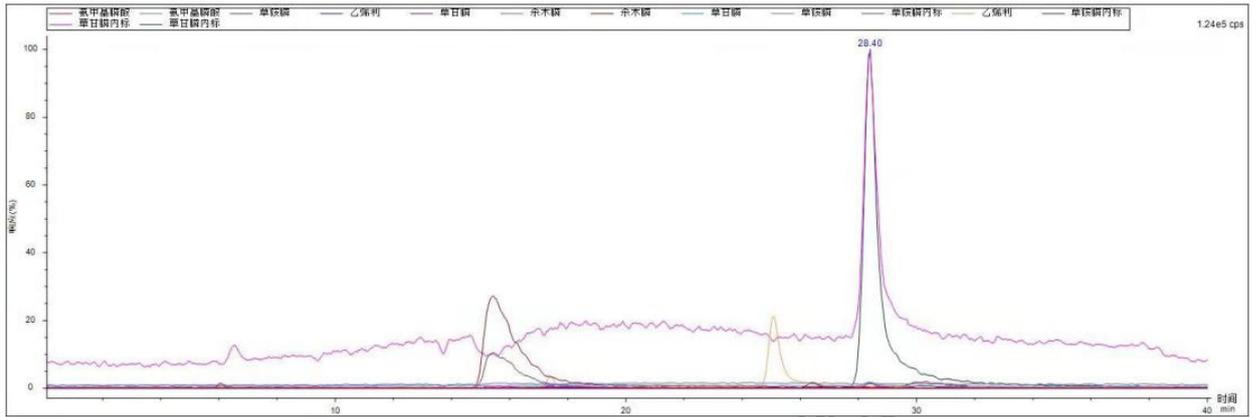


Fig. 1 Chromatogram of five organic phosphines and internal standard (lower limit of quantification)