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Determination of Sodium, Potassium, Calcium, Magnesium and Ammonium in Tobacco by Ion Chromatography

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A new method for the determination of sodium, potassium, calcium, magnesium and ammonium in tobacco by ion chromatography and sample preparation with matrix solid phase dispersion has been developed. The tobacco sample and C_{18} (1:4) were homogenized in a mortar and then packed into a cartridge. The sodium, potassium, calcium, magnesium and ammonium were eluted from the cartridge with 1.0 % hydrochloric acid and they were separated on an Ionpac® CS 16 (5.0 × 250 mm, 5 μm) cation ion exchange column with 0.03 mol/L methane sulfonic acid as mobile phase. The standard recoveries were in the range of 94-104 %. The relative standard deviations were less than 2.6 % (intra-day) and 3.3 % (inter-day). Results are satisfactory.

Key Words: Sodium, Potassium, Calcium, Magnesium, Ammonium, Tobacco, Ion chromatography, Matrix solid phase dispersion.

INTRODUCTION

Sodium, potassium, calcium, magnesium and ammonium are important components in tobacco. There is a close relationship between sodium, potassium, calcium, magnesium, ammonium and the quality of tobacco. Therefore, the determination of sodium, potassium, calcium, magnesium and ammonium in tobacco and cigarettes is important[1,2]. Sodium, potassium, calcium magnesium are commonly determined by spectrometric techniques such as atomic absorption spectrometry or inductively coupled plasma[3-5]. The ammonium cation in the same sample must be measured separately by a wet chemical technique such as colorimetry, titrimetry, or ammonia-selective electrode[6,7]. These methods may require a separate distillation step before ammonia can be determined. Ion chromatography (IC) in a single run can determine ammonium plus all of the important inorganic cations including sodium, potassium, magnesium and calcium[8-10].

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Matrix solid-phase dispersion (MSPD) has been successfully applied for the isolation of target molecules from biological matrices. The MSPD can incorporate the sample homogenization, cellular disruption, exhaustive extraction, fractionation and purification in a simple process. The procedure can considerably reduce the sample size and the solvent consumption[11-13]. However, the MSPD as sample preparation method for the determination of potassium, sodium, calcium, magnesium and ammonium had not been reported yet.

This paper describes the use of MSPD as sample preparation method and the ion chromatography with suppressed conductivity detection for the determination of sodium, potassium, calcium, magnesium and ammonium in tobacco. The results demonstrate that this method is simple, sensitive and selective.

EXPERIMENTAL

All solutions were prepared from analytical-reagent grade chemicals in reagent water (deionized water obtained from a Milli-Q50 water purification system with a specific resistance of 18.0 mv cm). Stock standard solutions of sodium, potassium, ammonium, magnesium and calcium with concentration of 1.0 mg mL^{-1} were purchased from the Chinese Standard Center. The stock standard solutions stored at 4 ºC are stable for at least 3 month. Working standard solutions were prepared fresh daily. Hydrochloric acid (1.0 %, v/v) was prepared by diluting the concentrated hydrochloric acid with water. The octadecylsilane (C_{18}) with particle size of 30-50 μm was purchased from Merck Company (Germany).

The IC system used in this work was Dionex (Sunnyvale, CA, USA) IC-900 system consisting of a gradient pump, automated sampler, eluent generator and conductivity detector. A Dionex PeakNet Chromatography Workstation was used for system control and data collection.

Chromatographic condition: A Dionex Ionpac® CS 16 (5 mm × 250 mm, 5 μm) analytical column and a CG16 (50 mm × 5 mm, 5 μm) guard column were used for separations. The mobile phase, 0.03 mol L^{-1} methane sulfonic acid (MSA) was generated on-line from reagent water with an eluent generator. All experiments were performed with the columns kept at temperature of 30 ºC. The CSRS-ULTRA operated at 100 mA in recycle mode and the injection volume is 20 mL. Under this condition, the chromatograms of the standard and tobacco sample were shown in Fig. 1.

Preparation of samples: The tobacco samples were dried at room temperature for constant weight and pulverized to 200 mesh. A 0.1 g of finely powdered sample was placed in a glass mortar containing 0.4 g of C_{18} (30-50 μm). The mixture was gently blended with a pestle. Once the mixture was homogenized, it was then transferred into the top of an 8 mm × 20 mm cartridge (Fig. 2) containing 0.2 g C_{18} (30-50 μm). The cartridge was eluted with 10 mL of 1% of hydrochloric acid to obtain the fraction containing sodium, potassium, ammonium, magnesium and calcium. This fraction was filtered through a 0.45 μm syringe filter and afforded to IC analysis.

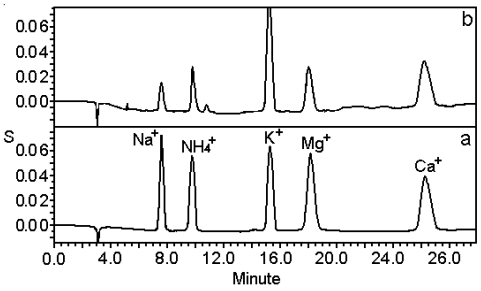

Fig. 1. Chromatogram of standard samples (a) and tobacco sample (b)

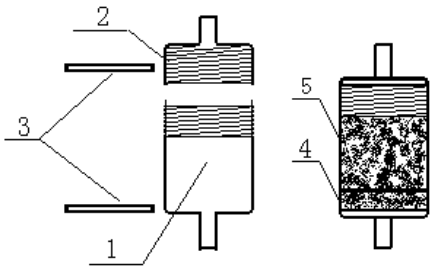

Fig. 2. The cartridge (1) Tube for fill in samples, (2) Screw cap for sealing the tube), (3) Sieve plate, (4) C_{18}, (5) The mixture of sample and C_{18}

RESULTS AND DISCUSSION

Matrix solid-phase dispersion (MSPD): The mechanism of MSPD includes sample homogenization, cellular disruption, exhaustive extraction, fractionation and purification in a simple process. Matrix solid-phase dispersion technology involves blending a small amount of matrix with an appropriate sorbent followed by washing and elution of compounds with a small volume of solvent. The procedure can considerably reduce the sample size and the solvent consumption. Therefore, MSPD was selected as sample preparation method in this work.

Different parameters that affect MSPD extraction such as dispersant agent, cleanup and eluent solvent were studied. The nonpolar solid phase (C_{18}, C_8, graphite carbon black, reversed-phase resin) were tested for matrix dispersion. High recoveries (> 95 %) of sodium, potassium, ammonium, magnesium and calcium were obtained when use C_{18} as dispersant agent. Therefore, the C_{18} (30-50 μm) was selected as dispersant agent. For eluting the sodium, potassium, ammonium, magnesium and calcium from the cartridge, 1 % of hydrochloric acid were used as eluant. For 0.1 g of tobacco sample, the results show that the use of 10 mL of eluant can be eluted the sodium, potassium, ammonium, magnesium and calcium from cartridge completely (recovery > 95 %). Therefore, 10 mL of 1 % hydrochloric acid were selected as eluant.

Optimal of ion chromatographic conditions: The initial ion chromatography method parameters investigated were based upon the published literature[8-10]. The IonPac CS 16 is a high-capacity cation-exchange column. The higher capacity improves performance for trace-level determinations of cations in high-ionic-strength matrices by extending the linear range and allowing resolution of higher concentration ratios of sodium and ammonium[8]. The results show that the sodium, potassium, ammonium, magnesium and calcium can achieve a baseline separation on Ionpac® CS 16 column using dilute methanesulfonic acid solution as mobile phase. Therefore, this column was selected in this experiment.

The experiments also indicate that the resolution of the sodium, potassium, ammonium, magnesium and calcium increase with the decrease of methane sulfonic acid concentration in mobile phase. However, long separation time need for the decrease of methane sulfonic acid concentration. Take resolution and separation time into consider, a 0.03 mol L^{-1} methane sulfonic acid was selected as mobile phase.

On the CS16 column, the retention time of cations does vary somewhat with temperature. The retention time of potassium is especially variable. This variability can be exploited to optimize selectivity among analytes, but could lead to misidentified peaks if the sample contains amines or other unknown compounds that elute near the standard cations. Therefore, we chose to use a constant temperature at 30 ºC to ensure the best possible reproducibility. Under these conditions, sodium, ammonium, potassium, magnesium and calcium are baseline resolved within 20 min.

Calibration graphs: Under the optimum conditions, the regression equations of sodium, potassium, ammonium, magnesium and calcium were established based on the standard samples injected and their peaks area. The limits of detection are calculated by the ratio of signal to noise (S/N = 3). The results were shown in Table-1.

TABLE-1
REGRESSION EQUATION, COEFFICIENT AND DETECT LIMIT

Components	Regression equation	Linear range (μg/mL)	Coefficient	Detect limit (μg/mL)
Sodium	A = 8.32 C + 0.157	0.2-110	r = 0.9995	0.04
Ammonium	A = 3.95 C - 0.048	0.4-150	r = 0.9996	0.06
Potassium	A = 12.4 C - 0.027	0.2-180	r = 0.9997	0.03
Magnesium	A = 14.5 C + 0.157	0.3-100	r = 0.9994	0.05
Calcium	A = 9.87 C - 0.058	0.4-150	r = 0.9993	0.06

C = μg/mL, A = Peak area.

Method recovery and precision: The recovery tests were carried out by adding sodium, potassium, ammonium, magnesium and calcium into the samples. Three different concentrations of markers (0.5, 2.0 and 5.0 mg) were chosed. The samples were prepared with above sample preparation method and afforded for IC analysis to calculate the amount of the sodium, potassium, calcium, magnesium and ammonium founded. The results shown that the recoveries (n=5) were ranged from 94-104 %. This method is high recovery.

The measurements of intra-day and inter-day variability (determination of the same samples for seven times) were utilized to determine the precision of the developed method. The results shown that the relative standard derivation of overall intra-day variations were less than 2.6 % and the relative standard derivation of inter-day variations were less than 3.3 %. This method is of high precision.

Conclusion

This method uses the IonPac CS16 column with a 0.03 mol L^{-1} MSA eluent and suppressed conductivity detection to determine inorganic cations and ammonium. The sodium, potassium, calcium, magnesium and ammonium in tobacco can be simultaneously in a single run. The matrix solid-phase dispersion (MSPD) was used as sample preparation method. MSPD combines both sample homogenization and extraction of the analyzed compounds in one step. It considerably reduced the sample size and the solvent consumption. The method precision and recovery are higher than that of traditional method. In a word, this method is rapid, high sensitive and selective and provides good reproducibility and accurateness for the quantification of sodium, potassium, calcium, magnesium and ammonium in tobacco samples.

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