Optimum Needle Materials of the Corona Discharge Electrode for Quantitative Analysis by Liquid Chromatography/Atmospheric Pressure Chemical Ionization-Mass Spectrometry

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(Received July 17, 1995)

Fourteen types of corona discharge needles made of different materials were used for high performance liquid chromatography/atmospheric pressure chemical ionization-quadrupole mass spectrometer (LC/APCI-QMS), and after a lapse of one hour and five hours from the start of the equipment, selected-ion monitoring determination of 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT) was made seven times repeatedly. Suitability as a discharge needle was judged by the total ($n=14$) relative standard deviation (T-RSD) of the quantitative determination value. T-RSD's of the iron needle, tin-plated iron needle, silver alloy needle, platinum alloy needle and stainless steel needle were 1–3%.

It could be elucidated from the scanning electron micrograph of the needle surface that suitability as a discharge needle was related to the stability of needle surface material against the corona discharge. The iron needle, having a small T-RSD was judged to be the most suitable as a corona discharge needle for quantitative analysis.

1. Introduction

Research on the direct coupling technique of liquid chromatography (LC) and mass spectrometry (MS) has been performed extensively. One of the most promising is the interface of the atmospheric pressure chemical ionization (APCI). LC-MS using APCI utilizing a corona discharge was reported by Carroll *et al.* in 1975.¹⁾ Conditions for LC measurement are generally applicable except for the mobile phase containing non-volatile salts. Most recent research and development can be applicable to the analyses of extensive materials.^{2–10)} A great interest has been paid for the instruments combining a LC/APCI interface and a quadrupole mass spectrometer (QMS). However, comparing with other detectors for LC, its reliability for quantitative analysis was insufficient because of the poor reproducibility, and thus the improvement of the performance is greatly needed.

At present, the nickel-plated iron needle and the stainless steel needle are used as the corona discharge needles for commercially available LC/APCI-QMS. Very few studies on the material of corona discharge needle for LC/APCI-MS have been carried out. Carroll *et al.* carried out research on corona discharge with platinum wire.¹⁾ Kato developed an assembly of plurality of needle electrodes using tungsten, rhenium or stainless steel as a needle material.¹¹⁾ It was reported that as discharges are generated at plural positions in their electrodes, the corona discharge was stabilized, and signal/noise ratio was improved. However, no definite data indicating the stability of a corona

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discharge can be found in Kato's report.¹¹⁾

This paper is to report the quantitative study of an LC/APCI-QMS instrument mounting fourteen kinds of needles with different materials for corona discharge. The optimum needle materials for corona discharge of LC/APCI-MS were judged from the values of total relative standard deviation (T-RSD) obtained by quantitative analyses ($n = 14$) of 3,5-di-*tert*-butyl-hydroxytoluene (BHT) determined seven times repeatedly after one hour and five hours from the start of the corona discharge.

Also reported is the fact elucidated from scanning electron micrographs that the suitability as the corona discharge needle is related to the stability of the needle surface against the corona discharge.

2. Experimental

2.1 Reagents

Most of the analytical grade reagents were obtained from Wako Pure Chemical Industries Ltd. A solution (5ppm) of BHT was prepared by dissolving BHT in methanol.

2.2 Apparatus

Hitachi Model M-1200H LC/APCI-QMS system and Hitachi Model S-800 scanning electron microscope were used.

2.3 Analytical conditions

The analytical conditions of LC/APCI-MS are summarized in Table 1.

2.4 Types of electrode needles for corona discharge

2.4.1 Standard needle Standard needle A (nickel-plated iron needle) is Japanese industrial standard (JIS) S3008 cotton needle No. 5, 0.84 mm in diameter, 45.5 mm in length and is made by electroplating an iron needle with nickel. This needle is used for the LC/APCI-QMS M-1200H system (Hitachi Ltd.).

2.4.2 Trial needle Thirteen kinds of needles having different surface materials

Table 1. Analytical Conditions for BHT, Reserpine, and Caffeine

Analyte	BHT	Reserpine	Caffeine
Amount (ng)	50	20	10
【MS】			
Mode	negative	positive	positive
Detected mass (m/z)	219	619	195
Drift volt. (V)	-30	60	40
Needle volt. (V)	-2700	3000	2700
Multiplier volt. (V)	1800	1800	1800
Nebulizer temp. (°C)	200	160	230
Desolvator temp. (°C)	400	360	420
Aperture 1 temp. (°C)	120	100	130
【HPLC】			
Column	TSK-gel ODS 150×6 mm id	TSK-gel ODS ←	CLC-ODS ←
Mobile phase	methanol	methanol	<div style="display: inline-block; vertical-align: middle;"> <div style="display: inline-block; vertical-align: middle; font-size: 2em; line-height: 1;">{</div> <div style="display: inline-block; vertical-align: middle;"> acetonitrile 200 methanol 50 water 750 </div> </div>
Flow rate (ml/min)	1.0	1.0	1.0
t_R (min)	4.5	4.8	4.7

were used (Table 2). Trial needles, B, C, D, E, F, and G were made by electroplating the iron needles. The iron needle corresponds to a needle that has not been electroplated of the standard needle A (Ni-Fe). Trial needles, I, J, K, L, M, and N were metal wire needles and were cut, ground, polished and finished into the conditions close to the standard needle A (Ni-Fe).

2.5 Maintenance of APCI interface

The corona discharge needle was exchanged for a new one each time after it was used, and at the same time, the APCI interface was cleaned.

2.6 Evaluation method of trial needle

Trial needles of all kinds were fitted to LC/APCI-MS, and quantitative analyses were made in the following way.

After one hour lapse from the start of the corona discharge, the quantitative analysis of BHT solution was made seven times. Next, after five hours lapse from the start of the corona discharge, the quantitative analysis of BHT was made seven times in the same way as that after one hour. From the value of peak area ($n=14$) measured at the times after one hour and five hours, total relative standard deviations (T-RSD) were calculated. Suitability, as a corona discharge needle, was judged from the T-RSD value of respective trial needles with respect to the value of standard needle A and from the statistical significant difference by equality of the two population variance test ($n=14$) between the standard needle A.

3. Results and Discussion

3.1 Calculated value of T-RSD

Until now, the reproducibility for LC-MS analyses was judged by the results of measurement made successively at a definite time. In order to investigate the time-course stability of LC-MS, the additional analysis at the five hours lapse after the start of the corona discharge was achieved.

Retention time (t_R) of BHT was 4.5 min, and it took about one hour to make quantitative seven-time repeated analyses including the data processing time. Corona discharge needles of all types were examined, and after one hour and five hours lapse, BHT of 50 ng was analyzed seven times respectively, and their T-RSD values were calculated from the peak areas (Table 2).

3.2 Shape of the tip of the needle electrodes

It was considered that the current of corona discharge depends on the shape or the curvature of the tip of needle. Therefore, the scanning electron micrographs of the shape of needles before and after the experiments were taken (Photo 1). One can see that the shape or the curvature of the needle tips did not changed markedly before and after the use. Thus, the change in the intensity of ion signals may not be due to the change of the shape of the needle tips.

3.3 Examples of the result using the standard needle A (Ni-plated iron)

The ion signal of BHT was found to decrease (see Table 3). As for reserpine, the measured area values decreased in the seventh analysis. And as for caffeine, the excellent repeatability was obtained up to the eighth analysis, but thereafter, the area values increased, and were stabilized again. The variation of these area values is

Table 2. Evaluation of the Trial Needles Based on the Total-Relative Standard Deviation (T-RSD)⁴ Calculated from the Results of Quantitative Analysis after One Hour and Five Hours Lapse from the Start of the Corona Discharge Calculated from the Peak Area ($n=14$)

Needle		A Ni-Fe ¹	B Ni, Au-Fe	C Au-Fe	D Ag-Fe	E Sn-Fe	F Cd-Fe	G Pb-Fe	H Fe	I 14Au	J Ag-alloy ²	K Pt-alloy ³	L Stainless	M Cu	N 18Au
Peak area															
1H	1	48001	33365	48153	43821	47207	43869	47378	62088	39965	50190	51392	54113	29100	— ⁶
	2	48812	34351	48787	41850	46926	43354	49541	63652	42644	50872	49444	54324	27028	
	3	52556	35564	47803	41572	48803	45236	47093	61750	41184	49568	49789	53271	26716	
	4	51202	35674	50642	40359	47508	42826	46473	61451	40641	50499	49302	53671	26745	
	5	49347	35767	49503	40251	48113	43858	47501	62372	42576	50000	48608	54283	16415	
	6	50474	32639	49807	41235	47915	44965	47565	62292	42948	50204	48010	55265	16471	
	7	50729	31928	51008	40527	49038	43396	47420	63042	42629	51061	49383	52726	24650	
5H	8	53565	31861	52712	47943	45919	47044	— ⁵	64118	43738	51756	52954	55371	— ⁷	— ⁶
	9	53282	33689	52447	45618	44999	47370		63116	43742	49539	51354	54770		
	10	55536	34691	52772	45180	44987	47820		64657	43239	51070	51643	55618		
	11	53714	36726	53395	47361	45611	47169		62665	45511	51328	51816	54430		
	12	55125	37756	55225	45992	44953	45524		63248	43607	49949	49597	54742		
	13	56594	39413	53577	46290	44992	45344		62759	44585	51576	48874	54842		
	14	54717	39605	54214	47667	44815	47504		62299	46662	50497	49607	58389		
$\bar{x}$		52404	35216	51432	43976	46556	45376	—	62822	43119	50579	50127	54701	—	—
σ_{n-1}		2683	2507	2372	2923	1549	1750		895	1799	715	1440	1329		
T-RSD ⁴ (%)		5.1	7.1	4.6	6.6	3.3*	3.9		1.4**	4.2	1.4**	2.9*	2.4**		

¹ Standard needle, Japanese industrial standard S3008; cotton needle.² Ag 95%, Cu 5%.³ Pt 90%, Pd 5%, Cu 5%.⁴ T-RSD ($n=14$) is based on the seven times analyses of BHT after one hour and five hours lapse from the start of corona discharge, respectively.⁵ Discontinued due to an offensive smell.⁶ The needle was bent by corona discharge, unable to continue.⁷ Not determined.* $p < 0.05$, ** $p < 0.01$: Statistical significant difference by equality of the two population variance (one-side) test ($n=14$) between the standard needle (Ni-Fe) and the trial needles, respectively.

Table 3. Examples of the Result Obtained by Selected-Ion Monitoring Analyses for BHT, Reserpine and Caffeine Using a Corona Discharge Needle of Nickel-Plated Iron (Standard Needle A)

Analyte		BHT	Reserpine	Caffeine
1H	Peak area			
	1	51998	21013	115382
	2	52437	18592	114902
	3	52262	17795	115700
	4	23959	19280	114963
	5	17648	19304	115275
	6	17038	19167	115338
5H	7	14903	20743	115976
	8	21082	43102	117121
	9	18667	49309	162919
	10	19222	52135	159648
	11	19014	52021	160589
	12	18028	48989	164176
	13	16528	46485	163452
	14	16062	48982	163974
Total	$\bar{x}$	25632	34066	135673
	σ_{n-1}	14583	15375	24108
	RSD (%)	56.9	45.1	17.8

originated from the fact that the surface conditions are different according to respective plated needles, such as the thickness of the plated layer, the state of adhesion of plating on the needle tips and the presence or absence of flaws on the plated surfaces. Because the plated surfaces were corroded gradually or rapidly by corona discharge, the intensity of ion signals changed depending on the experimental conditions.

3.4 Evaluation of the corona discharge needle

The plated-iron needles such as the needles B (Ni, Au-plated Fe), C (Au-plated Fe), D (Ag-plated Fe), and F (Cd-plated Fe) had a large T-RSD's compared with the standard needle A (Table 2). Plating made a metal film on the surface of the iron needle. The needle H (Fe) had larger peak areas (62,000), meanwhile, the needle B (Ni, Au-plated Fe) had smaller peak areas (35,000). It is considered that the sputtering of the surface materials caused by corona discharge leads to the signal instability, as the plating layer on the surface was corroded (Photo 1a-3). Among the plated-iron needles, only the needle E (Sn-plated Fe) has a smaller T-RSD value ($p < 0.05$) than that of the standard needle A (Ni-plated Fe). As the melting point of tin is 232°C which is lower than other metals used, the tip of the tin needle was easily melted by the discharge, and the plating layer was stripped off (Photo 1b-3), and corona discharge efficiency was improved. As the needle G (Pb-plated Fe) emitted an offensive smell from the beginning of the discharge, measurement was discontinued. The needle M (Cu) could not be used as a corona discharge needle for quantitative analysis (Table 2). As the needle N (grade 18 gold) having a large gold content was bent by the corona discharge. The needles, B (Ni, Au-plated Fe), C (Au-plated Fe), and I (14Au) have gold in the needle. Their peak area values increased during the measurement (Table 2). It was considered that the stability of gold against the corona discharge was poor (Photo 1c-3). The needles L (stainless

Photo 1. Scanning electron micrographs of the needle surface. Standard needle A (nickel-plated iron) a); needle E (tin-plated iron) b); C (gold-plated iron) c); needle L (stainless steel) d); needle H (iron) e) and trial needle J (silver alloy) f). 1, before use; 2, eight hours after the start of the discharged; 3, magnification of 2.

steel needle), H (iron needle), and J (silver alloy needle) had smaller T-RSD values ($p < 0.01$) than that of the standard needle A, and were judged as suitable for corona discharge needles. However, the stabilities of the needle L (Photo 1d-3) and J (Photo 1f-3) against corona discharge were much worse than the needle H (Photo 1e-3). When the needle H (iron needle) was used, the stability of the needle surface against the corona discharge was found to be satisfactory. Furthermore, a large value of peak area was obtained and the value of T-RSD of the needle H was the smallest. The iron needle was judged as most suitable for the corona discharge needle.

4. Conclusions

Out of fourteen types of corona discharge needles with different surface materials investigated, the iron needle was found to be the most suitable as a corona discharge needle for quantitative analysis for LC/APCI-MS.

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Keywords

LC/APCI-MS

Corona discharge needle

Scanning electron micrograph