樂盟季刊

Thermo Scientific iCAP Q ICP-MS 在藥物分析中的應用

The Thermo Scientific iCAP Q

關鍵字

USP <232>、USP <233>、ICP-MS、LC串聯ICP-MS、Cr物種分離、量測不確定度

前言

樂盟科技的應用團隊領先客戶需求與世界接軌，將化學分析中的經驗透過樂盟期刊公開發表，以提供客戶在儀器分析應用的參考依據。

本期主題為Thermo Scientific iCAP Q ICP-MS應用於藥物分析，以魚油和止痛藥為分析樣品，依循USP <232>和<233>，建立起分析方法與實驗數據，並且以LC串聯ICP-MS分析Cr(III)和Cr(VI)，延伸對元素物種型態分析的範疇。副刊則介紹實驗室中量測不確定度的評估程序。樂盟科技會定期舉辦AA、ICP-OES和ICP-MS的訓練教室，提供進階的訓練課程並協助客戶解決分析上的難題，更多的活動內容與時間列於本期刊內頁中。

本期內容

樂盟的精神宗旨

樂盟自成立初始，即秉持建立在地整體服務的精神，孜孜不懈的落實這項宗旨。樂盟公司在台北總部成立專屬訓練教室及實驗室，配備完善的實驗室周邊及新型的AA、ICP-OES和ICP-MS機種進行方法開發、流程實作(demo)，以服務客戶需求，伴隨市場同步進步。

積極建立銷售前、後的服務人力，售前會仔細傾聽客戶需求，為客戶量身打造最適的儀器需求內容。售後更會建立即時，不打烊的叫修，48小時到場的維修服務系統。目的即在讓客戶安心、放心及開心。

我們無論在 ppt 至 ppq 半導體的規格，或是食品衛生的法規，飲用水等等我們有深度的研究及全套的方法。

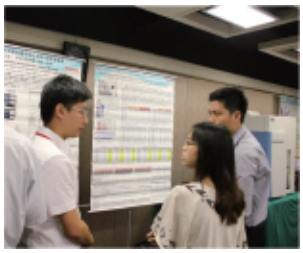
樂盟的一切努力，皆是為我們的客戶提高競爭力而存在，期待您享受樂盟的服務，一起茁壯堅實地穩健成長!

樂盟實驗室

樂盟會客bar檯

樂盟研討會

2013年6月樂盟科技新產品發表會，發表Thermo Scientific iCAP 7000 ICP-OES新產品，在台北、新竹和高雄的場次反應熱烈，總計有兩百多名客戶共襄盛舉。



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Thermo Scientific iCAP Q ICP-MS在藥物分析中的應用

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過去檢驗藥物中重金屬元素是利用與硫化物產生成色反應，再比對其濃度，但此方法元素回收率與專一性較不佳，因此成色法對重金屬分析至今已不敷使用。2013年美國藥典(United States Pharmacopeia, USP)發表藥典通則USP <232>和<233>，將於2014年開始實施。其中USP <232> 依照元素不純物對人體的影響程度與吸收途徑定立出人體每日最大可暴露量(Permissible daily exposure, PDE)，USP <233>則建議樣品前處理方法與分析儀器的選擇，並且為分析程序提出更為嚴謹的規範。

USP方法中推薦使用質譜分析儀器ICP-MS，Thermo Scientific iCAP Q ICP-MS 為多元素分析儀器，分析時間快速、高感度、低偵測極限和全新的去除干擾設計，能有效的解決在實驗中遇到的質量干擾的問題，在樣品量測中具有高度的準確性，能符合USP <232>及<233>所規定的藥品不純物的限量及分析程序。本章節利用Thermo Scientific iCAP Q ICP-MS分析魚油(Fish oil)和止痛藥(Metaxalone, MTAX)，分別使用微波消化和DMSO(Dimethyl sulfoxide)將樣品溶解後再上機分析，以驗證USP <232>和<233>所規範的測量方法。

樣品種類與前處理

本實驗分析兩種樣品：魚油和止痛劑，以比較兩種前處理方式的確效。

- 魚油(油狀樣品)：取0.2 g魚油於消化瓶中加入 6 ml 70% HNO_3 、3 ml 36% HCl 及 2 ml H_2O，放置hot plate上以90℃預消化30分鐘，再移入微波消化器中，待消化完全並冷卻後定量至50 ml。
- 止痛劑(粉末狀樣品)：取0.2 g止痛劑於離心管中，使用99.8% DMSO溶解定量至50 ml。

兩種樣品消化溶解前須加入USP <232>制定的15種元素及限量濃度(0.5、1和1.5 J)，以做為USP <233>方法之確效。

實驗分析與方法

實驗分析前必須參照USP <232>制定的15種元素As、Cd、Hg、Pb、V、Cr、Ni、Mo、Cu、Pt、Pd、Ru、Rh、Os 和 Ir的PDE ，或由客戶自訂較嚴苛的限量濃度，其 PDE 限量應考慮樣品製備過程中的稀釋倍數進行調整，例如魚油中的As 限量為 0.1 µg/g，在樣品消化過程中的稀釋倍率為250 倍(樣品0.2 g 消化後的最終定量至50 mL），因此As 的 PDE（“J”值）為0.4 ng/mL。算出每個元素的J值後配置檢量線溶液，線性範圍必須包含0.5、1及2J。兩種樣品的15種元素之限量濃度及檢量線濃度如表一。實驗流程中需加入5 ng/mL Sc、Y、In、Tb和Bi內標準品，以Y型管和樣品一起導入分析。

表一、兩種樣品15種元素之限量濃度及檢量線濃度

	Fish oil in HNO_3/HCl				MTAX in DMSO			
Element	Component Limits (µg/g)	STD-1 (0.5J) (ng/mL)	STD-2 (1J) (ng/mL)	STD-3 (2J) (ng/mL)	Component Limits (µg/g)	STD-1 (0.5J) (ng/mL)	STD-2 (1J) (ng/mL)	STD-3 (2J) (ng/mL)
Arsenic	0.1	0.2	0.4	0.8	0.75	0.15	0.3	0.6
Cadmium	0.1	0.2	0.4	0.8	12.5	2.5	5	10
Lead	0.1	0.2	0.4	0.8	2.5	0.5	1	2
Mercury	0.1	0.2	0.4	0.8	7.5	1.5	3	6
Vanadium	1	2	4	8	50	10	20	40
Molybdenum	1	2	4	8	50	10	20	40
Ruthenium	1	2	4	8	50	10	20	40
Rhodium	1	2	4	8	50	10	20	40
Palladium	1	2	4	8	50	10	20	40
Osmium	1	2	4	8	50	10	20	40
Iridium	1	2	4	8	50	10	20	40
Platinum	1	2	4	8	50	10	20	40
Nickel	5	10	20	40	250	50	100	200
Chromium	10	20	40	80	125	25	50	100
Copper	10	20	40	80	500	100	200	400

分析儀器與條件

藥物中不純物分析所使用的儀器為iCAP-Qc (Thermo Scientific)，可分析的質量範圍從4至250 amu。儀器進樣系統採用標準配備的電子式冰箱，可控制樣品進樣時的溫度，霧化器、霧化室及中心管管徑大小亦因樣品基質不同而選擇適當的材質。因樣品溶解的溶劑造成質量干擾，故儀器分析條件使用動能區隔(KED)模式分析，使用的碰撞氣體為氦氣，能有效地去除質量干擾，詳細的儀器進樣系統選擇及參數設定如表二。

表二、儀器參數設定

Operating Conditions	Water phase HNO_3/HCl	Organic Phase DMSO
Sample Introduction System		
Nebulizer	Quartz	PFA
Injector	Quartz 2.5mm ID	Quartz 1.0mm ID
Spray Chamber	Quartz, cyclonic	Quartz, cyclonic
Interface	Pt cone	Pt cone
Parameter		
Plasma mode	KED	KED
RF forward power (w)	1550	1350
Sampling depth (mm)	5	7.5
Nebulizer gas Flow (L/min)	1.03	0.688
Spray Chamber Temperature(℃)	2.73	20
He cell gas flow (mL/min)	4.2	4
Addition gas flow (mL/min)	none	O_2, 30

實驗數據及結果

1. 偵測極限

iCAP Q ICP-MS KED模式能有效地降低鹽酸基質所造成的同質量干擾，例如：$^{40}Ar^{35}Cl$對於^{75}As和$^{35}Cl^{16}O$對於^{51}V產生的干擾，去除干擾後檢量線線性r^2值皆大於0.998，並且具有低的偵測極限(Limit of detection, LOD)與背景值(BEC)。表三顯示兩種不同消化方法的LOD和BEC。

表三、目標元素於不同消化方法下其偵測極限和背景值(ppb)

	Fish Oil in HNO_3/HCl		MTAX in DMSO	
Mass	LOD	BEC	LOD	BEC
51V	0.81	0.089	0.372	0.122
52Cr	1.702	0.177	0.04	0.152
60Ni	0.044	0.011	0.029	0.132
63Cu	0.026	0.005	0.018	0.086
75As	0.015	0.012	0.028	0.005
98Mo	0.01	0.003	0.02	0.023
101Ru	0.002	0.001	0.005	0.005
103Rh	0.001	<0.001	0.002	0.008
106Pd	0.042	0.008	0.004	0.009
114Cd	0.001	0.002	0.011	0.003
192Os	0.006	0.002	0.017	0.026
193Ir	0.015	0.002	0.009	0.011
195Pt	0.001	<0.001	0.011	0.028
202Hg	0.022	0.002	0.033	0.013
208Pb	0.007	0.001	0.002	0.017

2. 樣品實際濃度

兩種藥物樣品實際濃度均小於USP <232>所制定的限量濃度如表四所示。

表四、樣品實際濃度(ppm)

	Fish Oil in HNO_3/HCl		MTAX in DMSO	
Mass	Component Limits	Sample Concentration	Component Limits	Sample Concentration
51V	1	< MDL	10	0.032
52Cr	10	0.460	25	0.027
60Ni	5	0.017	250	0.048
63Cu	10	0.028	100	0.099
75As	0.1	< MDL	0.75	0.005
98Mo	1	0.006	10	0.005
101Ru	1	< MDL	10	0.010
103Rh	1	< MDL	10	0.013
105Pd	1	< MDL	10	0.012
114Cd	1	0.002	12.5	0.004
188Os	1	0.017	10	0.023
193Ir	1	< MDL	10	0.012
195Pt	1	0.001	10	0.058
202Hg	0.1	0.001	7.5	0.011
208Pb	0.1	0.031	2.5	< MDL

3. 儀器偏移測試(Drift)

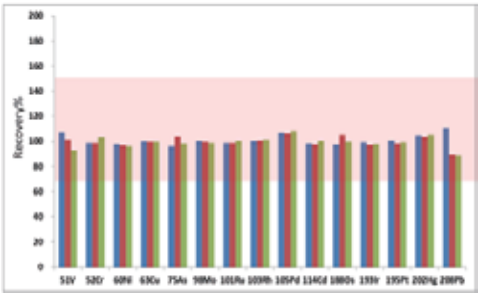
檢量線建立後及樣品分析完後皆須查核2 J的濃度，以計算樣品在分析前後儀器偏移的程度，相對誤差值須小於20%，此次分析結果以魚油樣品為例，儀器的偏移程度列於表五。

表五、儀器偏移測試

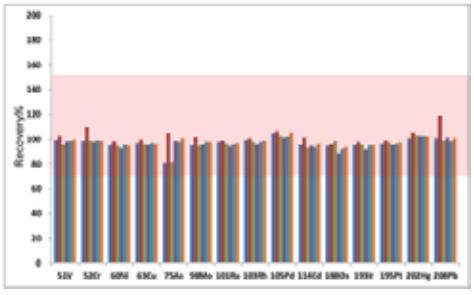
	Day 1			Day 2			
Mass	2J Before samples (ng/mL)	2J After samples (ng/mL)	Drift (%)	2J Before samples (ng/mL)	2J After samples (ng/mL)	Drift (%)	Limit
51V	8.02	7.42	**7.4**	7.99	7.39	**7.5**	< 20%
52Cr	79.74	76.31	**4.3**	79.83	75.03	**6**	< 20%
60Ni	39.80	37.97	**4.6**	39.75	38.63	**2.8**	< 20%
63Cu	79.96	76.35	**4.5**	79.62	76.36	**4.1**	< 20%
75As	0.80	0.80	**0.7**	0.80	0.78	**3.4**	< 20%
98Mo	7.97	7.61	**4.6**	8.01	7.55	**5.7**	< 20%
101Ru	8.02	7.46	**6.9**	7.97	7.64	**4.2**	< 20%
103Rh	8.03	7.45	**7.2**	7.96	7.67	**3.7**	< 20%
105Pd	7.88	8.33	**5.8**	8.13	9.10	**11.9**	< 20%
114Cd	0.81	0.84	**3.1**	0.80	0.79	**1.5**	< 20%
188Os	7.96	8.14	**2.3**	8.02	7.86	**2**	< 20%
193Ir	7.89	7.41	**6.1**	8.00	7.61	**4.8**	< 20%
195Pt	8.00	7.39	**7.6**	7.99	7.75	**3**	< 20%
202Hg	0.81	0.79	**2.2**	0.79	0.75	**6**	< 20%
208Pb	0.79	0.81	**1.8**	0.80	0.76	**5.1**	< 20%

4. 準確度測試(Accuracy Test)

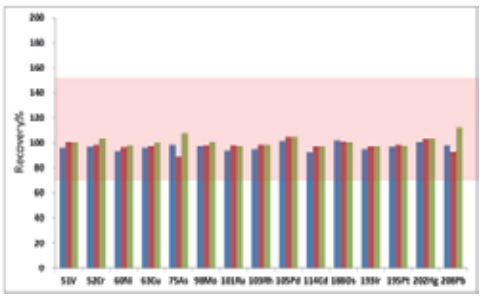
三個獨立樣品於樣品消化前各別加入0.5和1.5 J目標濃度，六個獨立樣品則添加1 J目標濃度，添加回收率需介於為70~150%。魚油樣品添加0.5、1和1.5J的回收率結果顯示於圖一~三。



圖一、魚油樣品添加0.5 J準確度測試



圖二、魚油樣品添加1 J準確度測試



圖三、魚油樣品添加1.5 J準確度測試

5.重覆性測試(Repeatability)

六個獨立的測試樣品，分別加入1 J的目標濃度，每個目標重金屬元素RSD不可超過20%，本次重複性結果顯示所有元素RSD均小於12%以下，如表六為魚油添加1 J，表七為MTAX添加1 J。

表六、魚油樣品添加1 J重覆性測試 (ng/mL)

Mass	Sample Spike 1 J-1	Sample Spike 1 J-2	Sample Spike 1 J-3	Sample Spike 1 J-4	Sample Spike 1 J-5	Sample Spike 1 J-6	Average	Std	RSD (%)	Recovery (%)
51V	3.70	3.84	3.56	3.64	3.65	3.73	3.69	0.09	2.56	98.91
52Cr	41.23	45.77	41.20	40.90	41.46	41.19	41.96	1.88	4.48	100.20
60Ni	19.00	19.66	18.96	18.65	19.17	18.97	19.07	0.33	1.75	94.99
63Cu	38.83	40.11	38.48	38.24	38.80	38.72	38.86	0.65	1.67	96.87
75As	0.32	0.42	0.33	0.39	0.39	0.40	0.38	0.04	11.10	93.79
98Mo	3.82	4.10	3.80	3.85	3.93	3.93	3.90	0.11	2.79	96.95
101Ru	3.91	3.95	3.86	3.77	3.85	3.88	3.87	0.06	1.61	96.69
103Rh	3.97	4.02	3.89	3.83	3.90	3.95	3.93	0.07	1.68	98.17
105Pd	4.17	4.24	4.10	4.01	4.07	4.20	4.13	0.09	2.10	103.90
114Cd	0.39	0.41	0.38	0.38	0.38	0.39	0.39	0.01	2.94	95.68
188Os	3.85	3.92	4.00	3.62	3.77	3.82	3.83	0.13	3.44	93.98
193Ir	3.80	3.89	3.83	3.69	3.79	3.80	3.80	0.07	1.76	95.14
195Pt	3.86	3.97	3.89	3.81	3.85	3.89	3.88	0.05	1.35	96.88
202Hg	0.41	0.43	0.42	0.42	0.42	0.41	0.42	0.01	1.51	103.00
208Pb	0.53	0.60	0.52	0.53	0.52	0.53	0.54	0.03	5.91	103.00

表七、MTAX樣品添加1 J重覆性測試 (ng/mL)

Mass	Sample Spike 1 J-1	Sample Spike 1 J-2	Sample Spike 1 J-3	Sample Spike 1 J-4	Sample Spike 1 J-5	Sample Spike 1 J-6	Average	Std	RSD (%)	Recovery (%)
51V	19.21	20.27	19.30	18.62	19.51	19.56	19.41	0.54	2.79	97.18
53Cr	51.07	50.91	51.34	50.74	49.83	50.39	50.71	0.54	1.07	101.40
58Ni	101.80	102.10	104.40	101.40	102.70	102.30	102.50	1.06	1.04	102.40
63Cu	205.10	205.30	208.10	202.70	206.60	205.20	205.50	1.81	0.88	102.70
75As	0.34	0.33	0.30	0.32	0.31	0.31	0.32	0.02	4.93	106.50
98Mo	19.97	20.41	20.29	19.65	20.23	20.08	20.10	0.27	1.34	100.50
101Ru	20.60	20.73	20.91	20.39	20.57	20.84	20.67	0.19	0.92	103.30
103Rh	18.82	18.91	19.01	18.51	18.87	18.91	18.84	0.17	0.92	94.14
106Pd	20.34	20.53	20.72	20.11	20.52	20.42	20.44	0.21	1.01	102.10
111Cd	5.09	5.05	5.12	4.99	4.97	5.00	5.04	0.06	1.20	100.70
192Os	20.82	20.78	20.61	20.73	20.82	20.50	20.71	0.13	0.62	103.40
193Ir	20.35	20.37	20.51	20.25	20.56	20.24	20.38	0.13	0.63	101.90
195Pt	20.20	19.99	20.10	19.72	20.22	20.11	20.06	0.18	0.92	100.00
202Hg	3.06	3.09	3.06	2.74	3.01	2.90	2.98	0.13	4.50	98.96
208Pb	1.03	1.01	1.02	1.02	1.03	1.03	1.02	0.01	0.70	102.70

表八、重現性測試

Mass	Actual (ng/mL)	Day 1 Mean (ng/mL)	Day 2 Mean (ng/mL)	RSD (%) (n=12)
51V	4	3.69	3.83	**2.9**
52Cr	40	41.96	43.11	**4.0**
60Ni	20	19.07	19.56	**2.3**
63Cu	40	38.86	39.54	**1.8**
75As	0.4	0.38	0.39	**7.9**
98Mo	4	3.90	3.97	**2.5**
101Ru	4	3.87	3.91	**1.8**
103Rh	4	3.93	3.99	**1.7**
105Pd	4	4.13	4.61	**5.9**
114Cd	0.4	0.39	0.39	**2.5**
188Os	4	3.83	3.32	**8.3**
193Ir	4	3.80	3.86	**1.8**
195Pt	4	3.88	3.94	**1.5**
202Hg	0.4	0.42	0.38	**4.7**
208Pb	0.4	0.54	0.53	**5.7**

6. 重現性測試(Ruggedness)

主要為測試同一樣品於不同天或不同分析人員或不同儀器的重覆性實驗，其RSD需小於25%。本次實驗為不同分析人員在不同天測試魚油樣品，結果顯示RSD均小於10%以下，詳細數據列於表八。

結論

利用iCAP Q ICP-MS，無論是魚油樣品(HNO_3/HCl)或是以DMSO有機溶解的藥品，在ICP-MS分析下具有低的偵測極限與背景值，樣品中的金屬不純物濃度亦符合USP <232>限量標準，並且能通過USP <233>分析程序所規範的儀器偏移、準確度、重複性與重現性測試，顯示出iCAP Q ICP-MS在USP <232>和<233>中，具有絕佳的適用性。

高效能液相層析儀串聯感應耦合電漿質譜儀在鉻物種分離之應用

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圖一、Thermo Scientific iCAP Q 與 Thermo Scientific Dionex Ultimate-3000

微量元素與人體的健康有著密切的關係，然而依據不同氧化數及化合物的組成，其毒性程度也有所不同，例如三價鉻為人體必須的微量元素，但六價鉻卻是對人類有害的致癌物質。只量測元素鉻總濃度已經無法代替各分量濃度，因此近年來對於物種型態的含量分析日益受到重視，尤其在食品、藥品和環境汙染安全分析中更是重要的一環。

然而在鉻物種分析上如何穩定不同價位的鉻離子是此實驗的關鍵，因為不同的鉻物種很容易受到樣品採集以及保存條件所影響，例如在較低的酸鹼值環境下，三價六價鉻的氧化還原電位增加，而在較高的酸鹼值環境下，會導致三價鉻沉澱。另外傳統的分析方法，例如比色法雖然簡便且快速，但其方法偵測極限較高，也易受到高濃度鐵離子干擾回收率測試也就不佳。因此需要一個具有高選擇性和高靈敏度的分析方法，而液相層析 (Liquid Chromatography，LC) 串聯感應耦合電漿質譜儀 (Inductively Coupled Plasma Mass Spectroscopy，ICP-MS)便能滿足此需求。首先由LC 先將樣品物種分離後再藉由ICP-MS分析，以達到靈敏度高、偵測極限低、干擾少的特性，已被廣泛地應用於元素物種型態分析上。

分析儀器與條件

本實驗使用 Thermo Scientific Dionex Ultimate-3000 高效能液相層析儀進行物種分離。儀器的管線路徑中完全無金屬材質，因此非常適合應用於微量金屬的物種分離。使用管住為 Thermo Scientific Dionex AG-7 陰離子交換管柱，雖然此為保護管柱，但它具有高效能的陰陽離子分離能力，因此能夠在三分鐘內將Cr(III)和Cr(VI)完全分離。

Thermo Scientific iCAP Q ICP-MS 做為高性能的偵測器，樣品經由管柱分離後與霧化器連接，依照進樣時間軸進行鉻的分析。Thermo Scientific iCAP Q ICP-MS 具有電子冰箱可控制霧化室的溫度在 -20～20℃ 之間，可依不同基質的樣品調控進樣溫度，另外方便拆裝的進樣系統，使得清洗保養更為快速，而儀器具備碰撞氣體的模式，可利用單一氣體(氦氣)有效地去除干擾，並且同時能保有測定時的高靈敏度，本實驗儀器參數設定如表一。

表一、儀器參數設定

Parameter	Value
ICP-MS	
Forward power	1550 W
Nebulizer gas	1.03 L/min
Injector	2 .5 mm I.D.
Cell gas flow	4.1 mL/min
Dwell time	200 ms
LC	
Column	Dionex AG-7 (4x50 mm)
Mobile phase	0.6 mmol EDTA(2Na)、0.07 mol NH_4NO_3 , use DIW set the volume to 1000 mL, adjusted to pH 7.1 with ammonia
Elution	Isocratic
Flow rate	1 mL/min
Injection volume	250 µL (自動進樣)
Duration	150 s

檢量線濃度

分別取1000 mg/L的Cr(III)和Cr(VI) 的標準品配置成1 mg/L的儲備溶液，Cr(III)的儲備溶液中需加入38 mg EDTA(2Na)，並以50℃水浴加熱三小時。配置檢量線時使用移動相稀釋，加入Cr(III)和Cr(VI) 1 mg/L的儲備溶液至0.05、0.1、0.5、1、5和10 µg/L，而試劑空白為移動相。

樣品前處理

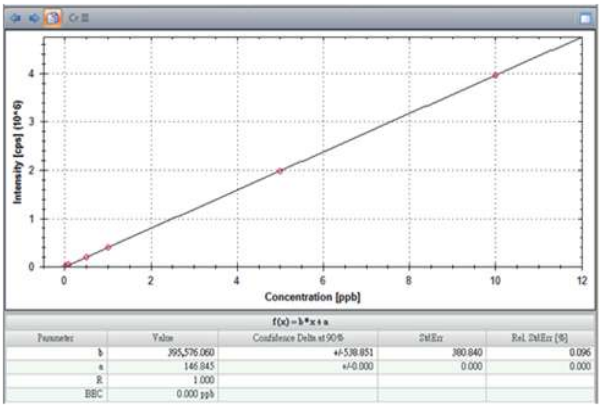
秤取0.5 g樣品加入0.07 mol HCl 25 ml 放置在水浴震盪器上，以 37℃ 萃取樣品一小時後再靜置一小時，之後氨水調整 pH=7.1，並以移動相定量至 50 ml 上機。

分析結果

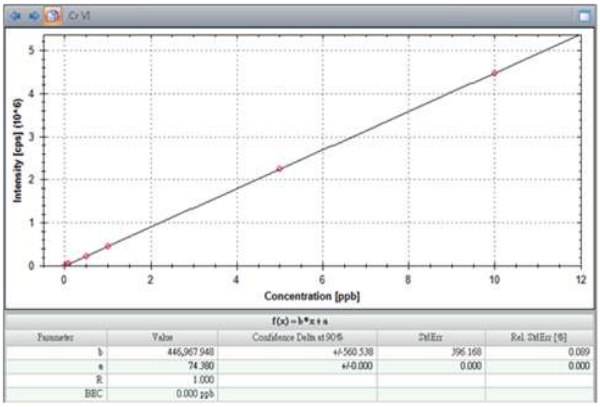
1. 檢量線線性

Cr(III)和Cr(VI)混和後建立檢量線的結果如圖一與圖二，顯示Cr(III)和Cr(VI)檢量線線性良好 ($r^2 > 0.999$) 且具有低的BEC (< 0.001 µg/L)，Cr(III) 1 µg/L具有4×10^5 cps，Cr(VI) 1 µg/L具有4.5×10^5 cps ，顯示此方法具有高靈敏度與低背景值。

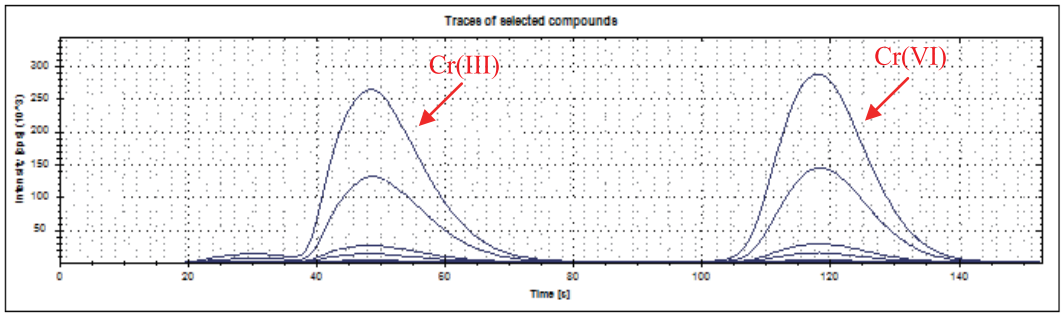
圖三顯示不同濃度標準品Cr(III)和Cr(VI)的分離效果，不同價數Cr並不會互相干擾，且分析時間僅需150秒。



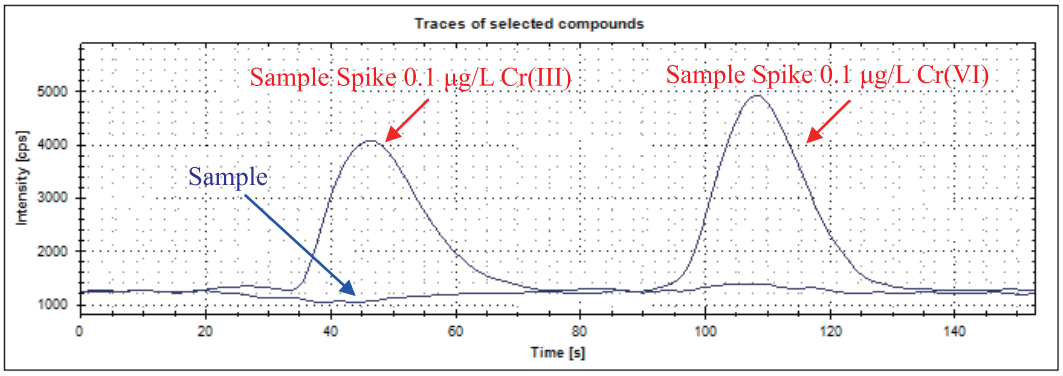
圖一、Cr(III)分離後的檢量線



圖二、 Cr(VI)分離後的檢量線



圖三、不同濃度標準品Cr(III)和Cr(VI)分離圖譜



圖四、樣品與樣品添加0.1 µg/L Cr(III)和Cr(VI)分離圖譜

2. 偵測極限

偵測極限以空白溶液重複分析7次計算得知Cr(III)和Cr(VI)偵測極限皆小於 1 ng/L 顯示此分離方法具有良好的偵測性能。

表一、偵測極限

Label	Cr (III) (cps)	Cr (VI) (cps)
BK-1	166	322
BK-2	227	138
BK-3	107	38
BK-4	36	301
BK-5	223	348
BK-6	139	153
BK-7	239	11
Average	162	187
SD	74	138
Slope	398954	448466
IDL (µg/L)	0.0006	0.0009

表二、樣品與樣品添加0.1 µg/L Cr(III)和Cr(VI)回收率測定

Label	Cr (III)	Cr (VI)
Sample	0.0004	0.0007
Sample Spike 0.1 µg/L	0.0968	0.1027
Recovery (%)	96.4	102.0

3. 實際樣品分析結果

實際樣品添加 0.1 µg/L計算回收率列於表二，Cr(III)和Cr(VI)回收介於95%~105%之間，顯示此方法有良好的加成性。圖四為樣品與樣品添加0.1 µg/L的分離圖譜，顯示添加元素有良好的分離性。

結論

本實驗利用高效能液相層析法結合感應耦合電漿質譜儀，可於 150 秒內有效的將 Cr(III) 與 Cr(VI) 完全分離，檢量線線性相關係數皆優於 0.999，而Cr(III) 與 Cr(VI) 的偵測極限皆可達到 1 ng/L。

量測不確定度的評估程序

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量測的結果通常不會是一個不變的數值，隨著測量環境、儀具設備、引用方法及人為因素等，都會產生不同的結果。量測不確定度(Uncertainty of Measurement)是一個估計區間，用以表示受測量值的分散程度，其大小決定了量測結果的使用價值。對於實驗室的量測運作上，量測結果如何與不同實驗室進行比較，量測不確定度的陳述為一項不可或缺的工具。本篇以ICP-OES 測量藥品中Pb含量，依循量測不確定度的評估程序將量測不確定因子量化加總，作為量測不確定度評估之說明。

量測不確定度評估程序

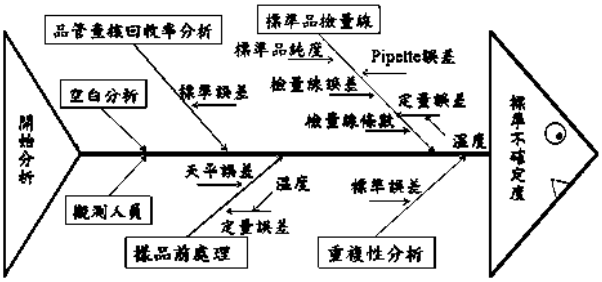
目前國際間通用的量測不確定評估方法，是依循國際標準組織（ISO）1995 年版「量測不確定度表示方式指引」中提供的評估程序。假設測試過程中每一個量測值、相關的參數值間都相互獨立，則可依以下六個程序估算之：

一、建立數學模式

在大多數的情況下，通常測量值Y是無法直接量測得到，而是透過受量測Y與輸入量Xi之間的函數關係，以$Y=f(X_1, X_2,\ldots, X_i)$方式表示。

二、確定量測系統中的不確定因子

常用的分析工具是以「特性要因圖（魚骨圖）」找出各種可能影響結果的不確定因子。標準不確定度為以一倍標準差表示量測結果的不確定度。



圖一、 不確定度因子

三、標準不確定度：A和B類評估方法

A 類標準不確定度(Tpye A Standard Uncertainty)：由一連串的觀測數列以統計分析方法計算求得的不確定度，必須實際重複量測以求得值。量測結果通常以重複量測多次之平均值表示，因此採用觀察結果平均數之標準差(而非單獨觀察結果之標準差)來表示標準不確定度。

$$s(x)=\sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i-\bar{x})^2}$$

平均數標準差(Standard Error，又稱標準誤)，即代表標準不確定度(Standard Uncertaninty)

$$s(\bar{x})=\frac{s}{\sqrt{n}}$$

表一為A類標準不確定度的評估實例，將樣品添加50 µg/L Pb的標準品，重複分析15次的數據列於表中，並計算出樣品平均值為50.37 µg/L，標準差為0.72，平均數標準差為0.19，平均數標準差即為A類評估之標準不確定度。

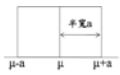
表一、樣品添加50 µg/L Pb重複測量15次的平均值、標準差和標準誤

	Pb (µg/L)
1	50.66
2	49.59
3	49.05
4	50.37
5	50.68
6	51.12
7	49.5
8	50.22
9	51.62
10	49.55
11	50.43
12	50.78
13	51.34
14	50.09
15	50.48
Average	50.37
SD	0.72
SE	0.19

B 類標準不確定度(Tpye B Standard Uncertainty)：當受測X之估計xi並非由重複觀測得到，其標準不確定度可用xi能變化的有關訊息來估算，稱為B類評估方式。此類評估方式乃以經驗上的機率分配來估算，如儀器操作規格或說明書、參考之標準或文件(如CNS、ISO)、實驗室先前累積之資訊、函數換算之計算等。

表二為B類標準不確定度評估之機率分配，矩形分配為最常使用的機率分配，如儀具的解析度、標準品純度等。三角形分配依量測或經驗可得知較集中於中心者，如定量容器、量瓶等。

表二、 B類標準不確定度的機率分配

矩形分配(Uniform or Rectangular Distribution)		
資料落在±a之間任何一點的機率皆相等	$u(x)=a/\sqrt{3}$	
三角形分配(Triangular Distribution)		
資料出現在中心值附近的機率高，且集中程度介於常態分配與矩形分配之間	$u(x)=a/\sqrt{6}$	

表三以50 ml 定量瓶為例，列出定量瓶之不確定度因子、不確定度與標準不確定度之計算，定量瓶的容差與標準偏差可由器皿的校正報告得知，而溫度變化不確定度計算如表下之說明，將不確定度除以機率分配可以求得標準不確定度。

表三、使用B類方法評估50 ml定量瓶的標準不確定度

Uncertainty factor X_i	Uncertainty	Probability distribution	Standard uncertainty $u(x_i)$	Sensitivity coeffcient C_i	$C_i \times u(x_i)$	$(C_i \times u(x_i))^2$
50 ml tolerance	0.06§	三角形分佈(√6)	0.0122	1	0.0122	0.00015
50 ml SD	0.017§	-	0.0170	1	0.0170	0.00029
50 ml temperature effect	0.1545*	矩形分佈(√3)	0.0892	1	0.0892	0.00796

§ 50 ml定量瓶容差和標準偏差的不確定度源自校正報告。
＊ 50 ml定量瓶溫度效應不確定度的計算方式
= 50 ml × 1.03*10-3 (盛裝有機溶劑的玻璃膨脹係數) × 3℃(溫度變化)) = 0.1545
☆ 50 ml 定量瓶組合標準不確定度 = √ 0.00015 + 0.00029 + 0.00796 = 0.0916

四、計算組合標準不確定度

組合標準不確定度是為組合各不同分量的標準不確定度。當量測結果由各分量依照不同的評估方法進行評估，且各分量之間的影響程度亦不一致，則需要透過數學運算的方式進組合。當輸入量之間不存在相關性時，組合標準不確定度表示如下：

$$u_c(y) = \sqrt{\sum_{i=1}^{N}\left[\frac{\partial f}{\partial x_i}\right]^2 u^2(x_i)}$$

式中每項$u(xi)$之靈敏系數 $\frac{\partial f}{\partial x_i}$ (也以Ci表示)係由偏微分方法計算得到，該係數說明當某一個值變動時對量測結果y影響的程度。

五、擴充不確定度與信心水準

如果不是要求特別嚴格的話，通常將測試系統視為一個常態分配的特性。亦即在95%信心水準下，使用擴充係數$k=2$來計算；在99%信心水準下，使用擴充係數$k=3$來計算。擴充不確定度U之估算為：

$$U = k\,u_c$$

六、不確定度結果闡明

說明在P%信賴水準下，擴充不確定度為U，或是在信心水準為P%下，信賴區間為$y-U$至$y+U$，並陳述所使用的規範及評估方法。為了使結果報告的呈現精簡易懂，在不影響量測結果信心下，ISO 建議不確定度應修整至適當的有效位數，一般而言為兩位有效位數。

表四依據實驗流程列出四大項的不確定度因子(前處理、標準品、檢量線和重複性分析)，將其取方根計算組合標準不確定度為0.61，在95%的信賴水準之下，擴充係數為2，因此擴充不確度為1.23。結果顯示Pb量測值與擴充不確定度為50.37 ± 1.23 μg/L 。

表四、不確定度因子評估列表

Uncertainty factor X_i	Probability distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient C_i	$C_i \times u(x_i)$	$C_i \times (u(x_i))^2$
一、前處理u_P		0.0916	1	0.0916	0.0084
1.天平不確定度u_{scal}	-	0.0002	1	0.0002	0.0000
2.定量瓶不確定度u_{fla}	-	0.0916	1	0.0916	0.0084
二、標準品u_S		0.0918	1	0.0918	0.0084
1.標準品純度u_{pure}	矩形分配(√3)	0.0058	1	0.0058	0.0000
2.pipette不確定度$u_{pipette}$	-	0.0005	1	0.0005	0.0000
3.定量瓶不確定度u_{fla}	-	0.0916	1	0.0916	0.0084
三、檢量線u_{cal}	-	0.5690	1	0.5690	0.3238
四、重複性分析u_R	t 分佈	0.1866	1	0.1866	0.0348
組合標準不確定度u_C=	0.61				
擴充係數k=	2				
擴充不確定度$U=k\times u_C$=	1.23	(95%信賴水準)			

結論

量測不確定度已成為實驗室重要的評估項目，藉由不確定度的評估，可了解到整體實驗室誤差的主要來源，並達到控制誤差提高量測的準確性的目的。

<下期預告>

鋰電池之分析

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科技產品日新月異，可攜式電子產品的需求也大幅提升，尤其是對於儲存能源的應用日趨重要。鋰電池發展促使科技大躍進，其可重覆充放電的特性，帶來可觀的經濟效應，相較於傳統電池如鉛酸、鎳鎘和鎳氫電池等，鋰電池具有低汙染、高工作電壓、高能量密度與高壽命等優勢，成為儲存能源的熱門商品。影響鋰電池效益的因素為其含碳比例與分布密度，以及其他主要元素的組成分。

Thermo Flash 2000元素分析儀可測量元素C、H、N、S和O，分析氣體只需He作為移動相氣體與O_2作為助燃氣體(分析O不需使用O_2)，每次分析的樣品量只需2~5 mg，低成本且操作簡單。

主要元素可藉由Thermo Scientific iCAP ICP-OES分析，其特色是可進行全光譜掃描，不用建立檢量線即可將樣品中的元素進行定性與半定量的分析，且主元素定量分析中，具有上萬條譜線供選擇，以避免光譜干擾。

下期樂盟季刊將介紹利用Thermo Flash 2000元素分析儀分析電池中的碳含量，Thermo Scientific iCAP ICP-OES分析主要元素的濃度，以上兩種儀器，可分析元素週期表中近八成的元素，對於鋰電池的組成分分析也就更顯得心應手。

近期活動

2013 年研討會	場次	日期	地點	主辦單位
樂盟科技 USP <232> <233>法規與實務操作		9 月 17 日	樂盟科技台北總公司	樂盟科技有限公司
樂盟科技 ICP-OES 訓練教室	台北	9 月 11 日	樂盟科技台北總公司	樂盟科技有限公司
	高雄	預計 10 月份	樂盟科技高雄分公司	
第十二屆台北國際儀器展		10 月 3 日至 10 月 6 日	台北世貿中心展覽大樓	台北市儀器商業同業公會
2013 中國化學年會		11 月 22 日至 11 月 24 日	國立暨南大學	中國化學會

詳細的活動以邀請函內文為主

Online Multi-elemental Monitoring of Environmental Atmospheric Gases with a Gas Exchange Device Coupled to the High Sensitivity Thermo Scientific iCAP Qs ICP-MS

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Application Note 43170

Key Words
Environmental gas monitoring, KED, Nuclear , Air, Pollution

Goal

To demonstrate real time multi-elemental analysis of environmental contaminants in air in using a gas exchange device coupled to the Thermo Scientific™ iCAP™ Qs ICP-MS.

Introduction

Environmental pollution is an immediate and growing concern. Environmental monitoring has become a key mechanism in determining how industrial activities and accidental contamination impact our water supplies, ecosystems and the air that we breathe. Strategic policies such as Clean Air for Europe (CAFE) and the United States Clean Air Act (CAA) for example, provide a framework of standards and objectives for the control of persistent pollutants that can damage health and the environment. Daughter directives within the CAFE program call for monitoring of nickel, arsenic, cadmium, mercury and lead. Of particular concern are fine particles with a diameter of less than 2.5 µm (PM2.5), which can penetrate deep into human bronchial tubes causing asthma and bronchitis. In China, where coal burning is still the biggest energy source and private car use is rapidly increasing, an estimated 70% of cities have PM2.5 levels above[1] the daily 75 µg PM2.5/m^3 Chinese National Air Quality Standard limit[2].

The Fukushima Daiichi nuclear power plant incident in 2011 demonstrated an immediate need for the monitoring of specific analytes in ambient air[3] in order to determine the distribution of radioactive materials in the environment, support remediation strategies and assess any possible subsequent threat to human health.

Current approaches for measuring radioactive contamination in the environment require the collection and preparation of soil and water samples and impingers or filtering for air sampling. These methods, however, cannot provide the real time results necessary for a meaningful assessment of current environmental conditions.

This application note evaluates the use of a gas exchange device (GED) coupled to the iCAP Qs ICP-MS for the direct analysis of atmospheric air (Figure 1). The GED overcomes problems in the direct analysis of air by ICP based techniques by exchanging atmospheric gases with argon which is compatible with the ICP ion source. Direct air sampling using the GED and on-line elemental analysis by high sensitivity ICP-MS therefore provides immediate information on airborne contamination.

The fast elemental scan speeds afforded by ICP-MS allow for the measurement of single particle events (SPE) that are seen as pulses in the signal intensity as they are processed by the ICP ion source. As air entrained elements are in particulate form, the ICP-MS based analysis of SPE can determine the number and even size of particles, therefore providing valuable information on elemental transport in the environment.

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Gas Exchange Device

Figure 1. Gas Exchange Device coupled to the Thermo Scientific iCAP Qs

The GED (J-SCIENCE LAB Co. Ltd., Kyoto Japan) consists of 2 inner tubes of 0.07 µm porous glass that act as a membrane and an outer body made of (PYREX™) glass (Figure 2). The gas sample is introduced into the central inner tube of the GED device and argon is introduced into the outer tube at 2 L/min using the GED internal mass flow controller.

As the particulate supporting gas travels along the inner tube, atmospheric gases diffuse out of the inner tube (indicated by the blue arrows in Figure 2) and argon diffuses from the outer tube into the inner tube (indicated by the yellow arrows). Ultimately, before the sample enters the plasma, the atmospheric gases have been replaced by argon while particulate matter from the sample remains.

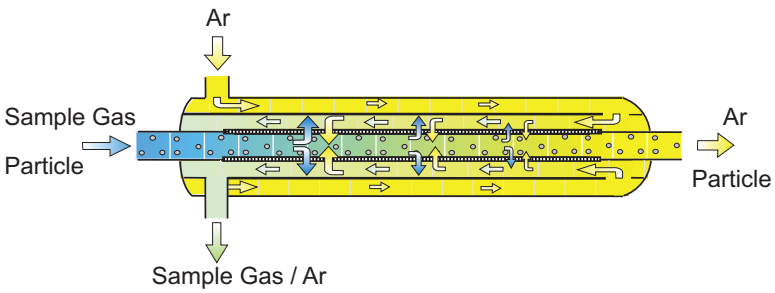

Figure 2. Principle of Gas Exchange Device

Instrument Configuration

A Thermo Scientific iCAP Qs ICP-MS was used for all measurements. The sample introduction kit consisted of a demountable quartz torch with a 2.0 mm ID sapphire injector. The spray chamber was removed and the exit line from the GED was attached directly to the injector using a PFA adapter. The instrument was operated in a single QCell mode, using kinetic energy discrimination (KED) with pure He as the collision gas. The use of pure He KED eliminates interferences, ensuring low backgrounds and maintains high sensitivity for the analytes measured.

Table 1. Instrument operating parameters

Parameter	Value
Sample gas	0.68 L/min
Air sampling rate	0.235 L/min
Auxiliary gas	0.8 L/min
Cool gas	14 L/min
Forward power	1550 W
Collision cell gas	He at 4.5 mL/min
KED barrier	3 V

Tuning, Sampling and Data Acquisition

The combined GED-ICP-MS system was optimized using a gas mixture of volatile ^{52}Cr, ^{95}Mo, and ^{184}W species generated by an Element Standards Gas Generator (ESGG) (J-SCIENCE LAB). The ESGG produces a continuous stream of elemental vapor in an argon gas flow that is introduced into the GED.

Ambient air was sampled via a TYGON® R3603 tube (i.d. 3.2mm, o.d. 6.4mm), approximately 15 m long. One end of the tube was connected directly to the GED; the other end was fed through an outside window, 10 m above ground. The argon sample gas flow of 0.68 L/min entrained the outside air through the tube and into the GED at a flow rate of 0.235 L/min. Sampling conditions are shown in Table 2.

Table 2. Sampling Conditions

Parameter	Value
Location	Bremen, Germany
Date, Time	18 Dec 2012, 9:30 am to 13:30 pm
Weather Conditions	Overcast, 6 °C, Wind: ENE 14 km/h

To determine optimal dwell times for the analysis of atmospheric particles, time resolved analyses of the target isotopes (^{66}Zn, ^{118}Sn, ^{121}Sb, ^{141}Pr, ^{205}Tl, $^{206, 207, 208}$Pb, ^{209}Bi and ^{238}U) were made using dwell times of 0.5, 1, 10 and 100 ms over a period of 300 s. In a subsequent 4 hour measurement of the outside air, a 10 ms dwell time was used for all isotopes.

Result and discussion

Ambient air was self-aspirated into the GED-ICP-MS and the target isotopes were analyzed at different dwell times as described. For analyses that intend to evaluate particle information, dwell times should be carefully optimized to favor the analysis of full SPEs. Dwell times that are too short, will measure sections of the SPE and dwell times that are too long will tend to measure multiple particle events in one scan.

Figure 3 (100 ms dwell) and Figure 4 (10 ms dwell) show time resolved scans for both an N_2 gas blank and an air sample. When comparing Figures 3 and 4, it is clear that 10 ms dwell time (higher scan frequency) provides improved discrimination between particle events and that individual events have a higher signal to noise ratio. At 100 ms dwell time, multiple events are captured together and averaged so that particle event information such as the number and intensity of events is lost.

Even shorter dwell times should further improve time resolution and dwell times of 0.5 and 1 ms were also evaluated. It was observed however, that shorter dwell times captured partial particle events and did not provide additional information compared to the 10 ms dwell time scans.

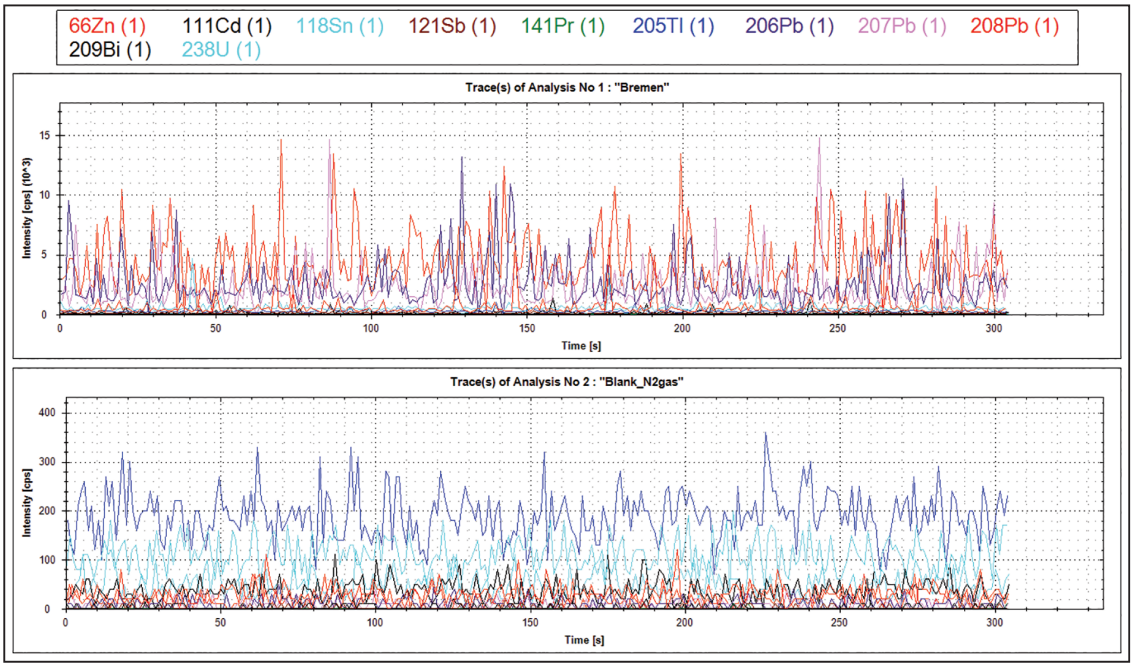

Figure 3. Time resolved scans for ambient air and an N_2 gas blank using a 100 ms dwell time.
Please note the different (vertical) intensity scales on the two scans

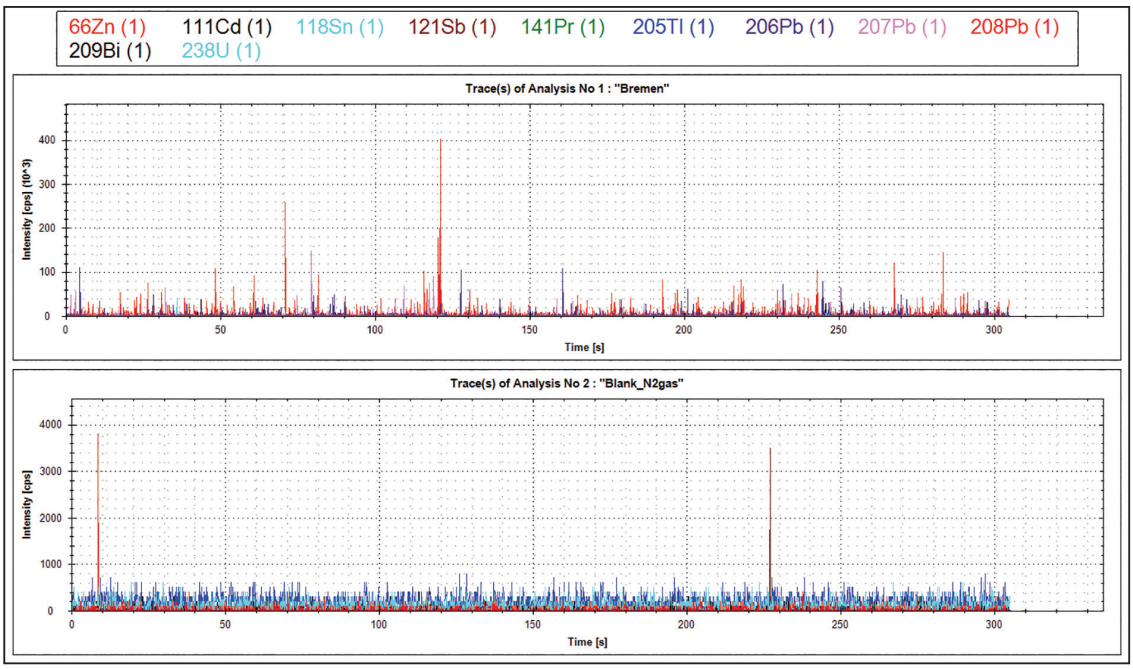

Figure 4. Time resolved scans for outside air and an N_2 gas blank using a 10 ms dwell time.
Please note the different (vertical) intensity scales on the two scans

A 10 ms dwell time was chosen for a longer term measurement of over 4 hours. Figure 5 shows a 30 minute section of the 4 hour monitoring period. Particle events for Zn, Pb and Bi are clearly shown.

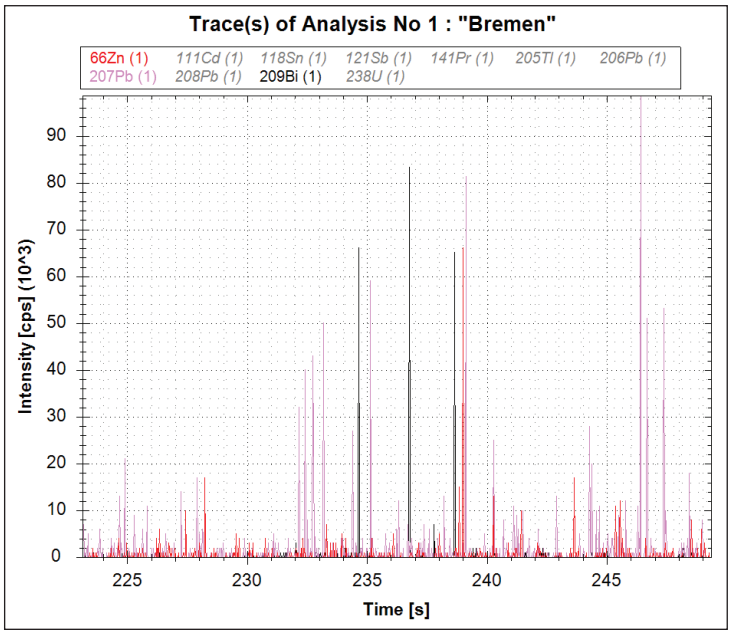

Figure 5. 30 minute section of the 4 hour air monitoring period

The environmental source of the particles observed in these analyses is practically impossible to determine as the particle trajectory travel distance is unknown. In this application, lead particles can be seen at regular intervals throughout the 4 hour period. The cycling and transport of lead in particulate matter is well documented, therefore lead particles are likely to occur in industrial and urban areas. For a more accurate evaluation of particle sources in air, further sampling points and baseline data regarding the geochemical cycling, potential sources and detailed environmental conditions at the time of sampling are required.

Conclusion

The Thermo Scientific iCAP Qs ICP-MS has demonstrated the high sensitivity and freedom from background interferences required for the measurement of particles in ambient air. The iCAP Qs ICP-MS has flexible scan times with a data buffer system capable of handling the large amounts of data acquired during long term *in-situ* analyses. QCell technology eliminates interferences whilst ensuring high sensitivity even for the lower mass isotopes thanks to its high transmission efficiency. A single mode KED approach could thus be employed for a number of isotopes across the mass range.

The use of a Gas Exchange Device coupled to the iCAP Qs ICP-MS is not limited to monitoring environmental air. Additional applications include monitoring a large range of gas samples such as specialty gases, semiconductor gases in the workplace, tobacco smoke and the presence of radionuclides.

Acknowledgement:

The gas exchange device and gas reaction system were provided by J-SCIENCE Lab., Japan

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Analysis of plating baths using the Thermo Scientific iCAP 7400 ICP-OES

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Key Words
Method of standard addition, plating baths, sulphuric acid levels

Goal
This application note describes the performance of the Thermo Scientific™ iCAP™ 7400 ICP-OES Duo analysing different elements in different types of plating baths. The duo viewing offers optimal method conditions using axial view for traces and radial view for major elements, and the pre-loaded template allows for rapid and simple method development.

Introduction
The plating of metal is an ancient technique, used for hundreds of years. It can be defined as the act of covering the surface of objects by depositing a metal on a conductive surface. This is typically carried out by immersing the object in a solution in which the metal ions are moved by an electric field. The applications are rather vast, ranging from the merely decorative, to the enhancement of the physical properties of the material being covered (i.e. to prevent corrosion, reduce friction, alter conductivity, or to improve characteristics such as hardness or durability). It is widely used in the production of jewellery pieces to achieve a silver or gold finish. Due to the ability to cover objects as small as an atom this technique has a high potential to be used in the nanotechnology area.

Manufactures frequently establish optimum specifications in order to guarantee maximum solution efficiency and uniformity of the plating solution. Plating solutions should be analysed regularly in order to maintain the recommended formulations and to prevent problems related to improper levels of bath constituents and contaminants. A current problem faced by the plating industry are gradual and continuous changes in pH and metal or cyanide content, leading to a significant decrease in efficiency. Some of the most common plating solutions and their main applications are presented in table 1.

Table 1. Plating solutions commonly used and their main applications

Plating Baths	Main applications
Alloy	Hardness improvement
Cadmium	Corrosion Resistance
Chrome	Decorative and industrial
Composite	Physical properties improvement
Golden	Jewellery manufacturing and electronics
Nickel	Decorative and corrosion resistance
Rhodium	Jewellery manufacturing
Silver	Jewellery manufacturing and electronics
Tin	Food processing and electronics
Zinc	Corrosion resistance

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There are several different methods that can be employed for the quantitative analysis of plating solutions; these are classified as volumetric, gravimetric or instrumental. Both volumetric and gravimetric methods are simple, accurate, and rapid and can be performed with common laboratory equipment. Nevertheless they only rely on chemical reactions instead of measuring the physical properties associated with the composition of the substance. Additionally, instrumental methods are far quicker and allow for the automatization of the analysis, leading to less mathematical errors and higher reproducibility.

A common instrumental technique is spectroscopic analysis, in particular inductively coupled plasma-optical emission spectroscopy (ICP-OES), which is used in the analysis of major components and trace contaminants in plating solutions. When using this technique there are some aspects that need to be taken into consideration, such as physical interferences (such as viscosity or surface tension) and chemical interferences. They can be overcome easily by sample dilution and accurate matrix matching.

The analysis of sulphuric acid (H_2SO_4) levels in plating baths is commonly performed by electroanalytical methods, specifically potentiometry. This is a simple and relatively low cost method but the sensitivity is limited at low concentrations, not allowing for accurate measurements in highly dilute solutions and it can also encounter a number of interferences. Maufacturers that use plating in their processes, are increasingly using ICP-OES instrumentation to quantify H_2SO_4 levels. This method allows for a rapid, sensitive and interference free measurement of sulphur, directly proportional to H_2SO_4, resulting in high accuracy even at low levels.

Instrumentation

The Thermo Scientific iCAP 7400 ICP-OES Duo was used for the analysis of a range of plating baths. This is a compact duo view ICP-OES instrument based on the innovative technologies of the iCAP 7000 Series ICP-OES spectrometers. The instrument achieves powerful analyte detection and provides a highly cost effective solution for routine analysis of liquids in laboratories with standard sample throughput requirements. The Thermo Scientific™ Qtegra™ Intelligent Scientific Data Solution™ (ISDS) incorporates several pre-loaded templates (see Figure 1) for common methods, simplifying normal method development and providing an option of immediate analysis.

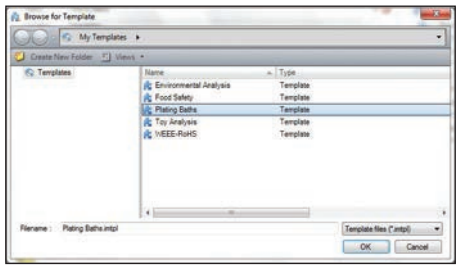

Figure 1. Plating Baths template selection

Sample and standard preparation

Elements analysed in each plating bath are presented in table 2. For the Chromium and Chromium & Aluminium baths the quantification of sulphur was performed in order to quantify the amount of H_2SO_4 in the samples.

Table 2. Elements analysed in each plating bath

Type of plating bath	Elements analysed
Chromium and ammonium fluoride (Cr & NH_4F)	Al, Cr, Zr
Nickel (Ni)	B, Ni
Chromium (Cr)	Fe, S
Chromium (Cr)	S
Chromium and aluminium (Cr & Al)	S

Quantification of the samples was made by Method of Standard Addition (MSA) to avoid any possible matrix effect. Standard addition calibration was prepared by spiking samples with traceable 1000mg/L aqueous, single element standards, to the concentrations listed in table 3. All solutions were made to 50 mL with ultra pure de-ionized water.

Table 3. Standard addition concentrations (mg/L)

Type of Plating Bath	Element	Blank	Standard 1	Standard 2	Standard 3
Cr & NH_4F	Al	0	1	2	-
	Cr	0	20	40	-
	Zr	0	50	100	-
Ni	B	0	5	10	-
	Ni	0	50	100	-
Cr	Fe	0	50	100	-
	S	0	50	100	-
Cr	S	0	50	100	150
Cr & Al	S	0	25	50	75

Method Development

A LabBook was created in Qtegra ISDS which contained the method parameters and standard concentrations as listed in this note. A standard sample introduction kit was used for the analysis. The instrument was calibrated and the samples analyzed in a single run. The method parameters are shown below in table 4.

Table 4. Method parameters

Parameter	Setting
Pump tubing	Sample Tygon® 1.016 mm Drain Tygon® 1.524 mm
Pump speed	50 rpm
Nebulizer	Glass concentric
Nebulizer gas flow	0.5 L/min
Spray chamber	Glass cyclonic
Center tube	2 mm
RF Power	1150 W
Coolant gas flow	12 L/min
Auxiliary gas flow	0.5 L/min
Exposure times	Low 10 sec High 5 sec

Results

The results obtained in the analysis of the different bath samples are shown in table 5. It is assumed that all of the sulphur present in the sample is in the form of H_2SO_4, therefore the results obtained for sulphur is multiplied by 3.06 [$M(H_2SO_4)\backslash M(S)=3.06$], in order to calculate the concentration of H_2SO_4. Results obtained for all the elements were within the expected range.

Table 5. Results of the analysis of the different plating baths. All concentrations are in mg/L.

Type of plating bath	Elements and wavelengths (nm)	Concentration found	Established concentration/range	Dilution factor*
Cr & NH_4F	Al 167.079	2.2	<10	100
	Cr 205.560	456.0	500	
	Cr 206.550	454.9		
	Cr 267.716	446.7		
	Zr 274.256	1504	1700	
	Zr 327.305	1486		
	Zr 339.198	1567		
	Zr 343.823	1689		
Ni	B 208.959	6380	<7000	1000
	B 249.678	6270		
	B 249.773	6150		
	Ni 221.647	95470	80000	
	Ni 231.604	94770		
Cr	Fe 259.837	2892	<5000	100
	Fe 259.940	2907		
	Fe 371.994	2823		
	S 180.731 (H_2SO_4)	1021.6 (3126)	2500 – 3000 (H_2SO_4)	
	S 182.034 (H_2SO_4)	1035.0 (3167)		
	S 182.624 (H_2SO_4)	983.7 (3010)		
Cr	S 180.731 (H_2SO_4)	85.6 (2020.3)	2250 – 2500 (H_2SO_4)	10
	S 182.034 (H_2SO_4)	79.4 (2429.6)		
	S 182.624 (H_2SO_4)	74.2 (2271.7)		
Cr & Al	S 180.731 (H_2SO_4)	5.7 (35.1)	<150 (H_2SO_4)	2
	S 182.034 (H_2SO_4)	7.5 (45.9)		
	S 182.624 (H_2SO_4)	7.5 (45.9)		

* All dilutions were prepared using ultra pure water.

Concentration ranges were established by the manufacturers taking into account the concentrations usually found in these types of plating baths to obtain maximum efficiency. This gives the plating operators the status of the bath simplifying the assessment of how the bath composition evolves overtime.

Conclusion

The analysis of plating baths, specifically those that require the analysis of sulphuric acid, is rapid and highly sensitive when using the Thermo Scientific iCAP 7400 ICP-OES in conjunction with the Qtegra ISDS. This enables the accurate quantification of metals and sulphuric acid content, while the powerful, easy to use iCAP 7400 ICP-OES allows both experienced and inexperienced users alike to vastly reduce the method development time required for these sample types, resulting in cost effective analyses.

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