质量歧视因子及光电离截面测量

MDF & PICS Calculation

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1. Fundamental Concepts

In Cool's paper, the signals can be written as:

$$S_i(T) = CP_i(T)\sigma_i(E)D_i\Phi_p(E)F(k,T,P) \quad (1)$$

Which $S_i(T)$ is the integration of mass peak without dimension , $\Phi_p(E)$ means photon intensity which unit is photons/sec and has been corrected by quantum efficiency:

$$\Phi_p(E)(\text{unit}:\text{photons/ sec}) = \frac{I_P(E)(\text{unit}:\text{A})/q_e(\text{unit}:C)}{\eta(E)(\text{unit}:\text{none})} \quad (2)$$

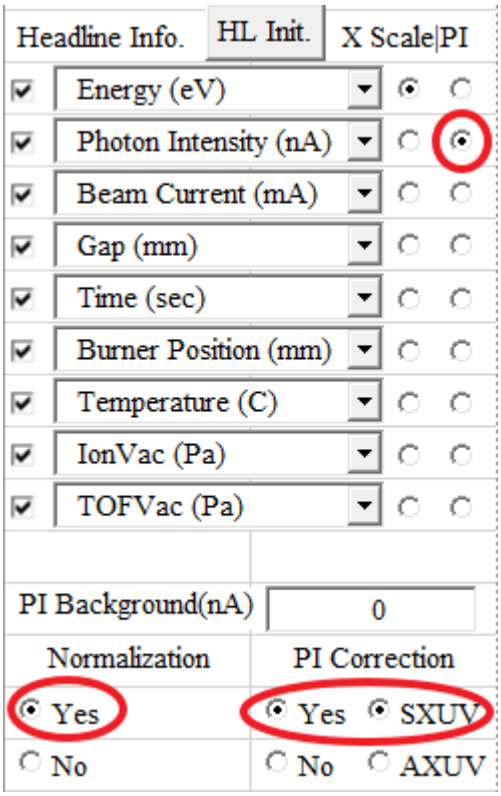
While $I_p(E)$ is photon current detected by photodiode which unit is A, $\eta(E)$ is quantum efficiency of photodiode.

There are two ways to obtain Normalized and Corrected Signal $S_i(T, NC_{Normalized\&Corrected})$.

a. Photon current information existed in spectra files：

$$\frac{S_i(\mathrm{T})}{\Phi_\mathrm{p}(\mathrm{E})} = \frac{S_i(\mathrm{T})}{\frac{I_\mathrm{p}(\mathrm{E})/q_e}{\eta(E)}} = S_i(T, NC_{Normalized\&Corrected}) = CP_i(T)\sigma_\mathrm{i}(\mathrm{E})\,\mathrm{D_i F(k,T,P)} \quad (3)$$

In the integration calculation program, if you've got the photon intensity data in the spectra file, you can select the 2nd headline as PI, and set Yes for Normalization and Yes, SXUV for PI Correction. Then you can get the result of $\frac{S_i(T)}{I_P(E)/q_e/\eta(E)}$.

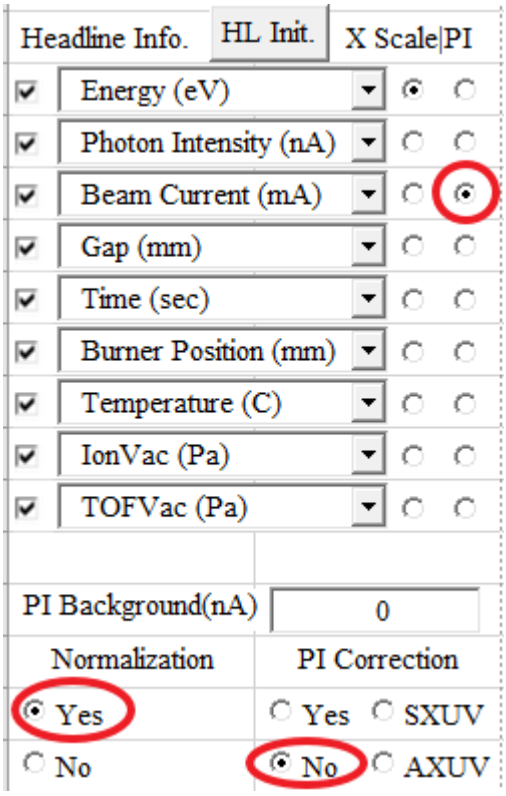


b. Photon current information is not existed in spectra files

If you did not got the photon intensity data in the spectra file, the signal $S_i(T)$ should be normalized by beam current first to get $\frac{S_i(T)}{BC(t_1)}$, then normalized by standard photon flux $\frac{\Phi_p(E)}{BC(t_0)}$ which has been corrected by quantum efficiency $\eta(E)$. $BC(t)$ is electron beam current of synchrotron storage ring which unit is mA, $BC(t_1)$ meant the current during experiment, $BC(t_0)$ meant the current when standard photon flux experiment carried on. $\frac{\Phi_p(E)}{BC(t_0)}$ can be obtained in another manual (Zhongyue Zhou, Xuewei Du, JiuZhong Yang, Beamline Optics of BL03U at NSRL (Version 20191011). http://flame.nsrl.ustc.edu.cn/database/?data=Training. National Synchrotron Radiation Laboratory, Hefei, China. (2019)).

$$\frac{S_i(\mathrm{T})}{BC(t_1)} = CP_i(T)\sigma_i(\mathrm{E})\,\mathrm{D_i}\,\frac{\Phi_p(\mathrm{E})}{BC(t_0)}\,\mathrm{F(k,T,P)}$$
$$\frac{\dfrac{S_i(\mathrm{T})}{BC(t_1)}}{\dfrac{\Phi_p(\mathrm{E})}{BC(t_0)}} = S_i(T, NC_{Normalized\,\&Corrected}) = CP_i(T)\sigma_i(\mathrm{E})\,\mathrm{D_i F(k,T,P)} \quad (4)$$

In the integration calculation program, you can select the 3rd headline as PI, and set Yes for Normalization and No for PI Correction. Then you can get the result of $\frac{S_i(T)}{BC(t_1)}$.Next, you can use the additional standard photon intensity data $\frac{\Phi_p(\mathrm{E})}{BC(t_0)}$ to calculate $\frac{\frac{S_i(\mathrm{T})}{BC(t_1)}}{\frac{\Phi_p(\mathrm{E})}{BC(t_0)}} = S_i(T, NC_{Normalized\,\&Corrected})$.



Then we can compare $S_i(T, NC)$ and $S_j(T, NC)$, the equation will be:

$$\frac{S_i(T, NC)}{S_j(T, NC)} = \frac{X_i(T)}{X_j(T)}\frac{\sigma_i(E)}{\sigma_j(E)}\frac{D_i}{D_j} \quad (5)$$

$$\frac{D_i}{D_j} = \frac{X_j(T)}{X_i(T)} \frac{S_i(T,NC)}{\sigma_i(E)} \frac{\sigma_j(E)}{S_j(T,NC)} \quad (6)$$

$$\sigma_i(E) = S_i(T,NC) \frac{X_j(T)}{X_i(T)} \frac{\sigma_j(E)}{S_j(T,NC)} \frac{D_j}{D_i} \quad (7)$$

2. How to determine MDF(Mass Discrimination Factor)

2.1. If shape of curve of $S_i(T, NC_{Normalized\&Corrected})$ fits well with $\sigma_i(E)$

According to equation (6), we can estimate a factor with error by comparing the $S_i(T,NC)$ curve and $\sigma_i(E)$ curve, and again for specie j. The MDF $\frac{D_i}{D_j}$ could be calculated then.

2.2. If shape of curve of $S_i(T, NC_{Normalized\&Corrected})$ doesn't fit well with $\sigma_i(E)$

If the signal shape of curve and $\sigma_i(E)$ curve doesn't fit well, just calculate each point of $\frac{D_i}{D_j}$ and plot, then evaluate the proper value.

2.3. MDF of different facilities

Table 1 MDF of different facilities

Catalysis Facility	5 Torr (400μm orifice nozzle)	$\left(\frac{x}{30}\right)^{0.36267}$
Combustion Chemistry Facility	30 Torr (350μm orifice nozzle)	$\left(\frac{x}{30}\right)^{0.75148}$
	150 Torr (150μm orifice nozzle)	$\left(\frac{x}{30}\right)^{0.76155}$
	760 Torr (80μm orifice nozzle)	$\left(\frac{x}{30}\right)^{0.77897}$

2.3.1. Catalysis Facility with 1 differential stage (1st stage expansion and ionization)

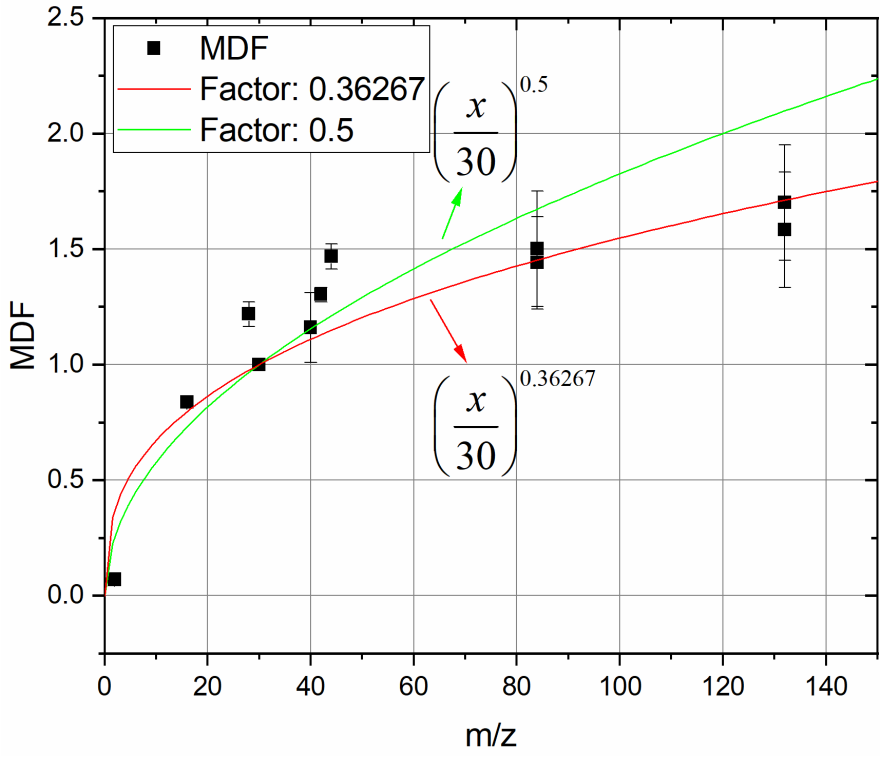


Figure 1 MDF of Catalysis Facility (5.0 Torr, 400 μm orifice nozzle)

2.3.2. Combustion Chemistry Facility with 2 differential stages (1st stage expansion and 2nd stage expansion and ionization)

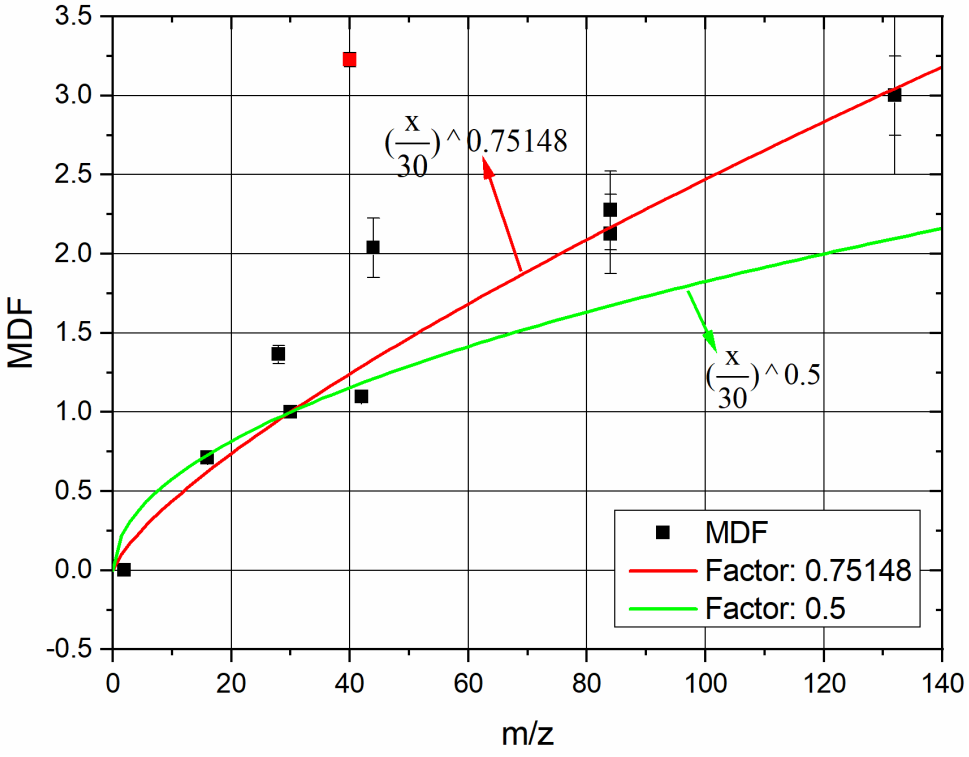


Figure 2 MDF of Combustion Chemistry Facility (30.0 Torr, 350 μm orifice nozzle)

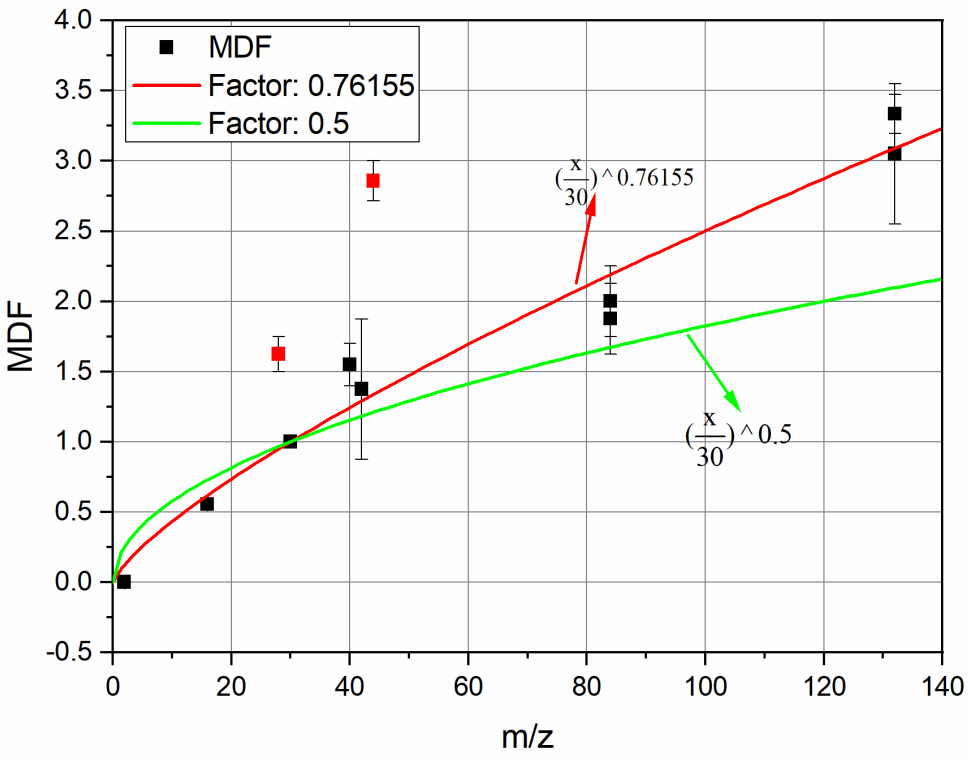


Figure 3 MDF of Combustion Chemistry Facility (150 Torr, 150 µm orifice nozzle)

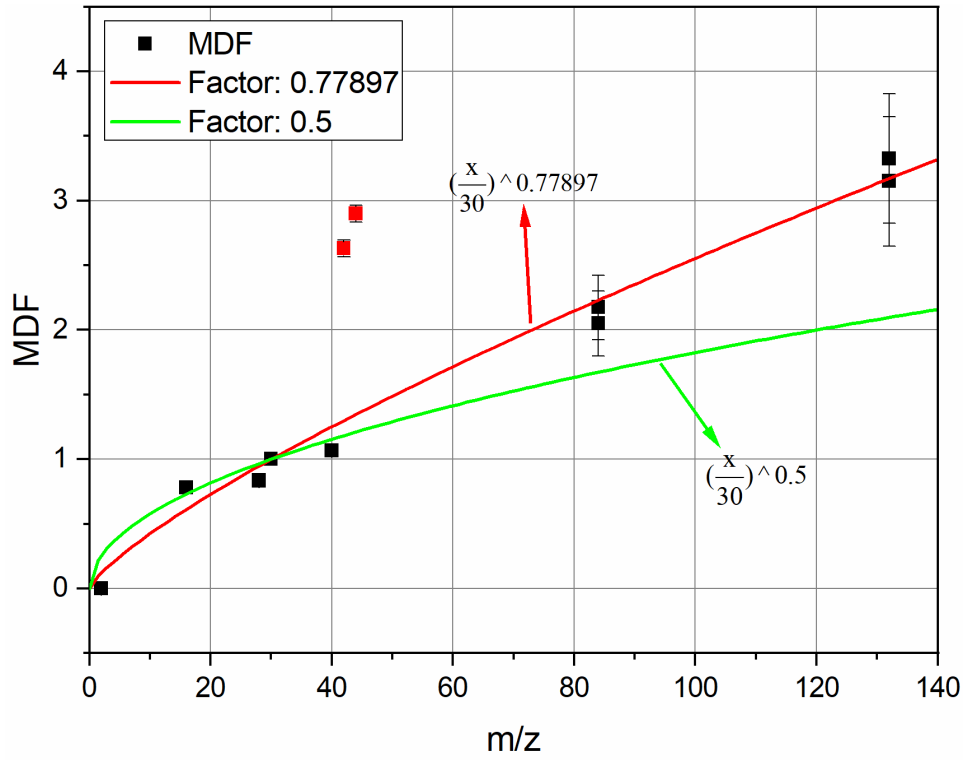


Figure 4 MDF of Combustion Chemistry Facility (760 Torr, 80 µm orifice nozzle)

3. How to calculate PICS(Photoionization Cross Section)

3.1. PICS Calculation

According to equation(7), If shape of curve of $S_j(T, NC)$ fits well with $\sigma_j(E)$, similar method in section 2.1 could be used to calculate and estimate the PICS of $\sigma_i(E)$.

If not, method in section 2.2 could be used to evaluate the PICS of $\sigma_i(E)$.

4. 基本公式及概念

Cool 的文献里，质谱信号可以表示为：

$$S_i(T) = CP_i(T)\sigma_i(E)D_i\Phi_p(E)F(k,T,P) \quad (8)$$

其中，$S_i(T)$ 是质谱峰积分强度，无量纲，$\Phi_p(E)$ 表示的是绝对光通量，单位 photons/sec，$\Phi_p(E)$ 可以表示成：

$$\Phi_p(E)(\text{unit}:\text{photons/ sec}) = \frac{I_P(E)(\text{unit}:\text{A})/q_e(\text{unit}:C)}{\eta(E)(\text{unit}:\text{none})} \quad (9)$$

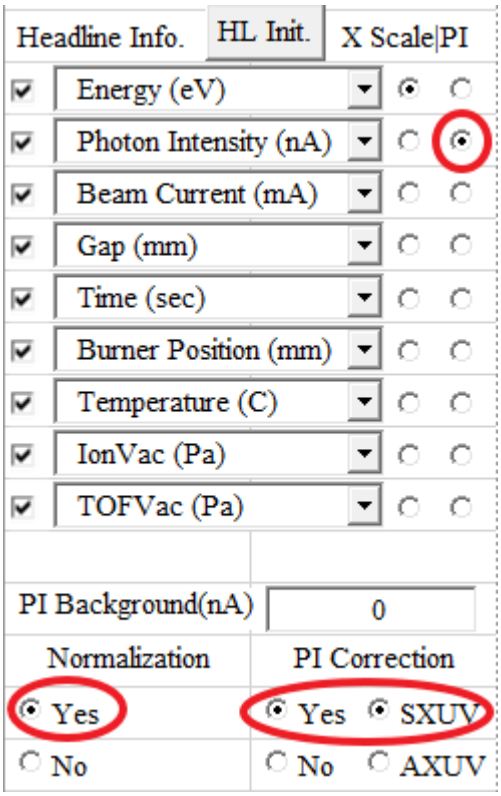
$I_{\mathrm{p}}(E)$ 是光电二极管测量得到的光电流强度，单位 A，$\eta(E)$ 是光电二极管的量子产率，无量纲。

因此，可以使用两种方式得到校正后的信号 $S_i(T, NC_{Normalized\&Corrected})$。

一种是实验时有光强信息：

$$\frac{S_i(\mathrm{T})}{\Phi_{\mathrm{p}}(\mathrm{E})} = \frac{S_i(\mathrm{T})}{\frac{I_{\mathrm{p}}(\mathrm{E})/q_e}{\eta(E)}} = S_i(T, NC_{Normalized\&Corrected}) = CP_i(T)\sigma_{\mathrm{i}}(\mathrm{E})\,\mathrm{D_i F(k,T,P)} \quad (10)$$

具体操作上，在积分程序界面，如果质谱文件中有光强信息，那么在头部航信息设置区域，选择第二行为光强，归一化和光强校正分别选择”是”、”是”和”SXUV”，则可得到 $\frac{S_i(T)}{I_P(E)/q_e/\eta(E)} = \frac{S_i(\mathrm{T})}{\Phi_{\mathrm{p}}(\mathrm{E})}$。

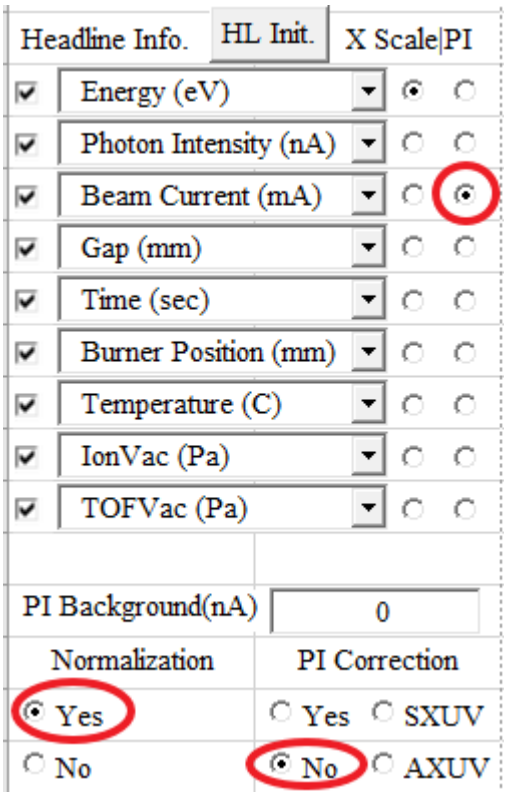


另一种情况是实验时未获得光强信息，可以先经流强归一化 $\frac{S_i(T)}{BC(t_1)}$ 再用标准光通量 $\frac{\Phi_p(E)}{BC(t_0)}$ 归一化。式中，$BC(t_1)$ 表示实验时的束流强度，单位 mA。$BC(t_0)$ 是测量标准光通量时的束流强度。$\frac{\Phi_p(E)}{BC(t_0)}$ 表示经过流强归一化并且考虑不同能量量子产率校正的标准光通量，可以通过后续单独测量不同光子能量下的光强再除以流强归一化，或者调用之前的标准光通量曲线（按 300 mA 流强归一化，参考《BL03U 光束线参数》文档中标准光通量 $\frac{\Phi_p(E)}{BC(t_0)}$ 部分）：

$$\begin{aligned}&\frac{S_i(\mathrm{T})}{BC(t_1)}=CP_i(T)\sigma_i(\mathrm{E})\,\mathrm{D_i}\,\frac{\Phi_p(\mathrm{E})}{BC(t_0)}\mathrm{F(k,T,P)}\\&\frac{\frac{S_i(\mathrm{T})}{BC(t_1)}}{\frac{\Phi_p(\mathrm{E})}{BC(t_0)}}=S_i(T,NC_{Normalized\,\&Corrected})=CP_i(T)\sigma_i(\mathrm{E})\,\mathrm{D_i}\mathrm{F(k,T,P)}\end{aligned}\qquad(11)$$

具体操作上，在积分程序界面，如果质谱文件中没有光强信息，那么在头部

航信息设置区域，选择第三行束流强度为光强，归一化和光强校正分别选择”是”、”否”，则可得到 $\frac{S_i(T)}{BC(t_1)}$。然后再与标准光强 $\frac{\Phi_p(E)}{BC(t_0)}$ 运算，得到 $\frac{\frac{S_i(T)}{BC(t_1)}}{\frac{\Phi_p(E)}{BC(t_0)}} = S_i(T, NC_{Normalized\&Corrected})$。



物种 i 和 j 相除得到：

$$\frac{S_i(T,NC)}{S_j(T,NC)} = \frac{X_i(T)}{X_j(T)}\frac{\sigma_i(E)}{\sigma_j(E)}\frac{D_i}{D_j} \quad (12)$$

$$\frac{D_i}{D_j} = \frac{X_j(T)}{X_i(T)}\frac{S_i(T,NC)}{\sigma_i(E)}\frac{\sigma_j(E)}{S_j(T,NC)} \quad (13)$$

$$\sigma_i(E) = S_i(T,NC)\frac{X_j(T)}{X_i(T)}\frac{\sigma_j(E)}{S_j(T,NC)}\frac{D_j}{D_i} \quad (14)$$

5. MDF 测量

5.1. 校正后的信号 $S_i(T, NC_{Normalized\&Corrected})$ 与截面 $\sigma_i(E)$ 线型符合对比法

根据公式(13)，扫描能量，得到 PIE 曲线 $S_i(T, NC)$ 和 $S_j(T, NC)$，使用 Origin 里的 Analysis->Mathematics->Simple Curve Math 功能，将信号的线型除以一个常数，分别与文献值 σ_i(E) 和 σ_j(E) 对比，得到 $\frac{S(T, NC)}{\sigma(E)}$ 的比值并估算误差，最后计算 $\frac{D_i}{D_j}$。

5.2. 校正后的信号 $S_i(T, NC_{Normalized\&Corrected})$ 与截面 $\sigma_i(E)$ 线型不符合情况

如果线型相差较大，则用 Origin 里的 Analysis->Mathematics->Simple Curve Math 功能直接对 $S(T, NC)$ 和 σ(E) 两条曲线进行数学运算，得到 $\frac{S(T, NC)}{\sigma(E)}$ 曲线。再直接对 $\frac{S_i(T, NC)}{\sigma_i(E)}$ 和 $\frac{S_j(T, NC)}{\sigma_j(E)}$ 两条曲线进行数学运算，得到 $\frac{D_i}{D_j}$ 以及误差。

5.3. 若干装置的 MDF

Table 2　若干装置的 MDF

催化装置 Catalysis Facility	5 Torr (400μm orifice nozzle)	$\left(\frac{x}{30}\right)^{0.36267}$
燃烧化学装置 Combustion Chemistry Facility	30 Torr (350μm orifice nozzle)	$\left(\frac{x}{30}\right)^{0.75148}$
	150 Torr (150μm orifice nozzle)	$\left(\frac{x}{30}\right)^{0.76155}$
	760 Torr (80μm orifice nozzle)	$\left(\frac{x}{30}\right)^{0.77897}$

5.3.1. 催化装置（一级差分直接电离）

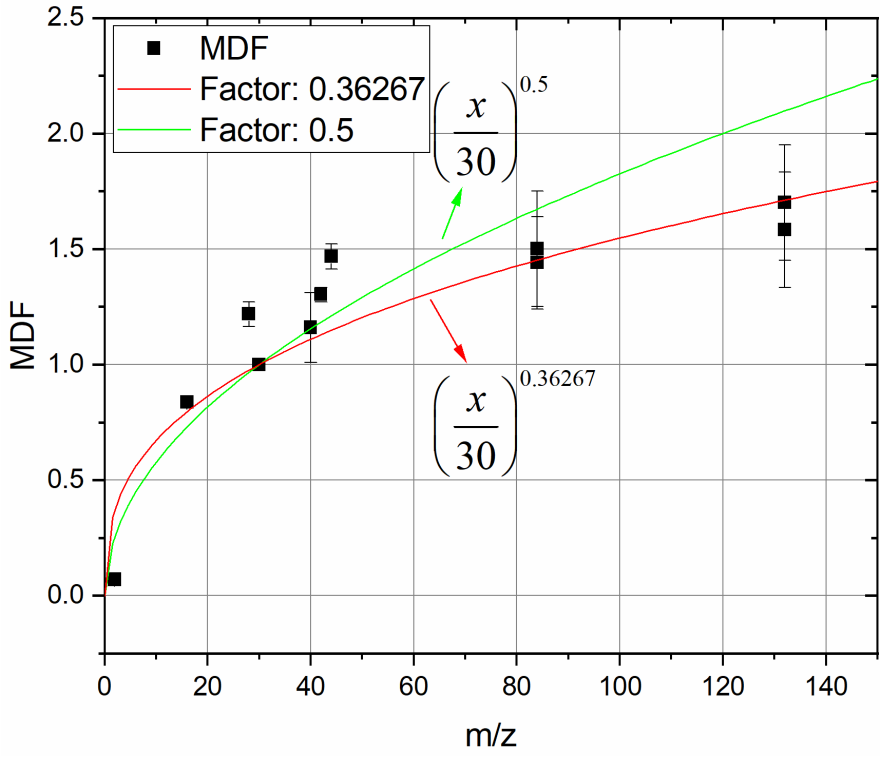


Figure 5 MDF of Catalysis Facility (5.0 Torr, 400 μm orifice nozzle)

5.3.2. 燃烧化学实验装置（二级差分，一级超声膨胀，二级膨胀及电离）

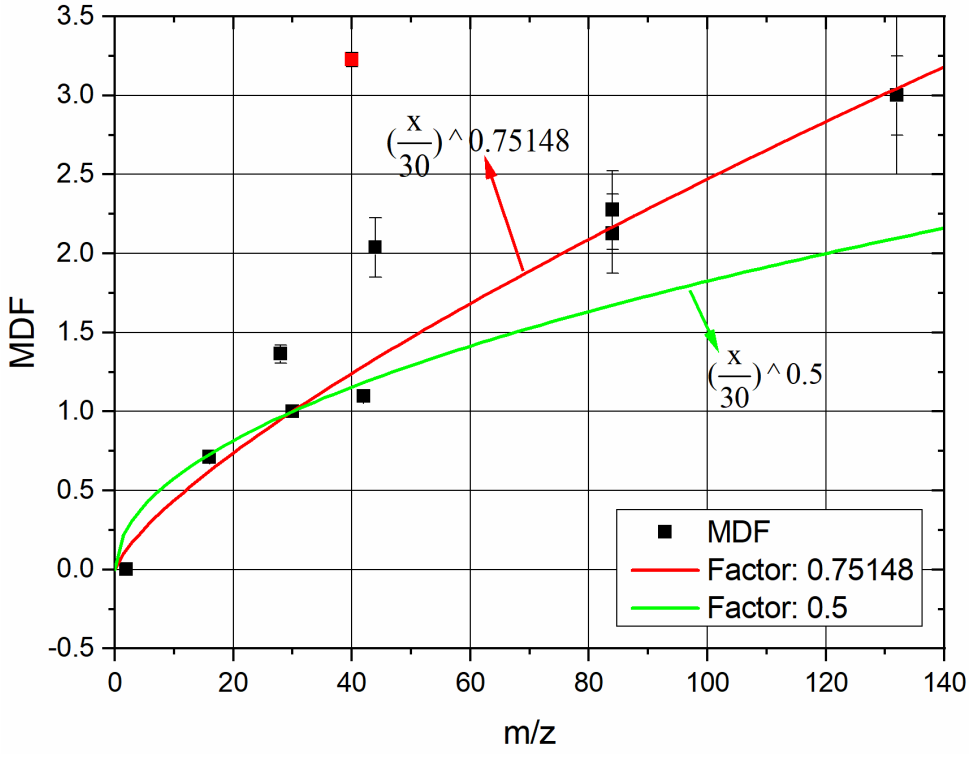


Figure 6 MDF of Combustion Chemistry Facility (30.0 Torr, 350 μm orifice nozzle)

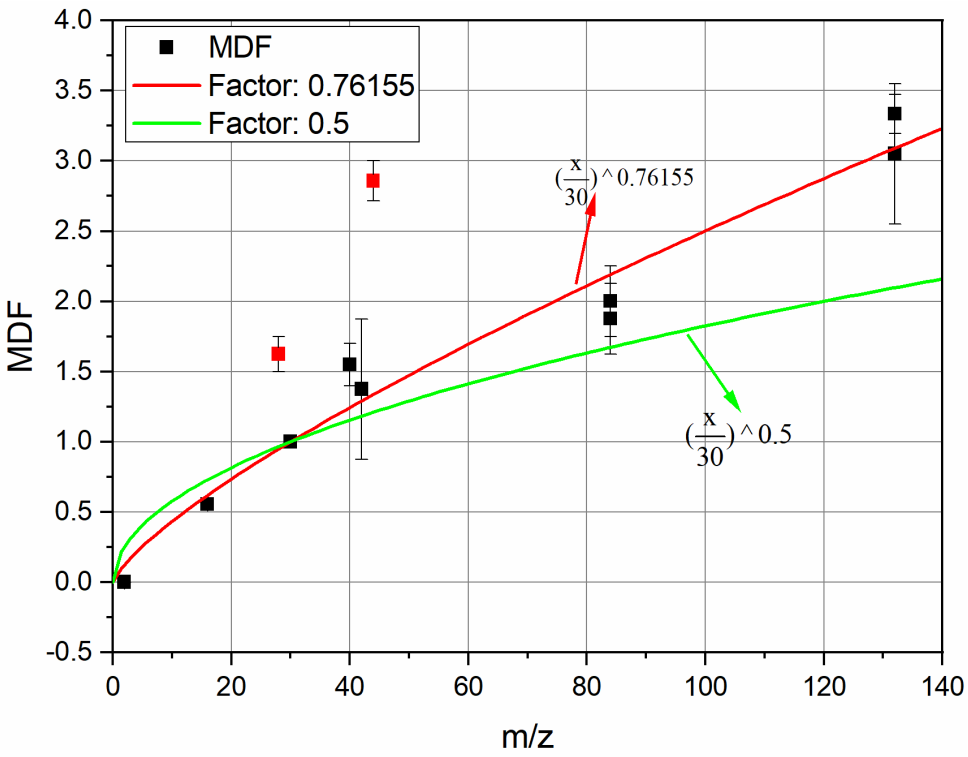


Figure 7 MDF of Combustion Chemistry Facility (150 Torr, 150 µm orifice nozzle)

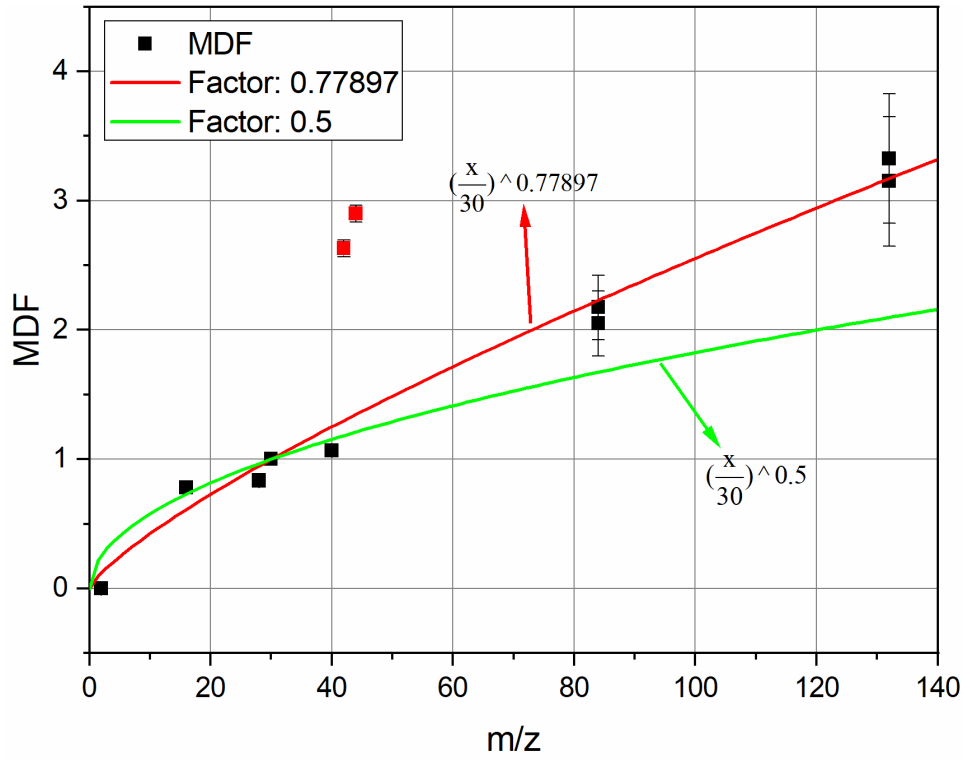


Figure 8 MDF of Combustion Chemistry Facility (760 Torr, 80 µm orifice nozzle)

6. PICS 测量

6.1. 计算 PICS

根据公式(14)，求得质量歧视因子后，即可利用已知电离截面测量未知电离截面。

此处，仍可按照线型相符及不符的方法进行计算。优先使用线型相符方法。