

GCMS QP-2010 Plus测定PVC和橡胶中的16种PAHs

No.GCMS-0014

摘要：本文详细介绍了GCMS QP-2010 Plus测定PVC和橡胶制品中16种PAHs样品的前处理方法，线性方程，重现性和回收率。

多环芳烃(简称PAHs)是指由两个或两个以上苯环以线状、角状或簇状排列的化合物。PAHs最突出的特性是致癌、致畸及致突变性，并且致癌性随着苯环数的增加而增加。当PAHs与—NO、—OH、—NH₂等发生作用时，会生成致癌性更强的PAHs衍生物。有机物的不完全燃烧，煤/油/气/烟草/烤肉、木炭、原油、木馏油、焦油、药物、染料、塑料、橡胶、农药、发动机、发电机都会产生PAHs。除了电动工具外，很多电器产品中都存在PAHs。目前，大多数国家都将多环芳烃列为环境监测的重要内容之一，中国政府列出的“中国环境优先监测黑名单”中包括7种PAHs；美国环保总署1979年确定了16种PAHs作为优先监测污染物，分别是萘、苊、苊烯、芴、菲、葱、荧葱、芘、苯并[a]葱、屈、苯并[b]荧葱、苯并[k]荧葱、苯并[a]芘、茚并[1, 2, 3-cd]芘、二苯并[a, h]葱、苯并[g, h, i]芘。现在德国政府强制规定所有在德国出售的电动工具必须经过检验其中不得含有过量的PAHs。

关键词：GCMS PVC 橡胶制品 多环芳烃(PAHs)

仪器

GCMS-QP2010 Plus

分析条件

进样口温度： 280℃
 进样方式： 不分流进样
 流量控制方式： 线速度控制 (44.4cm/min)
 色谱柱： RTX-5ms, 30m × 0.25mm × 0.25 μ m
 柱温度： 50℃(3min)–10℃/min–200℃–5℃/min –280℃(8min)
 接口温度： 280℃
 离子源温度： 250℃
 扫描方式 (Scan)： m/z 45 ~ 400

样品处理

参照EPA 8270。PVC材料和橡胶粉碎后,称取1.0g,加入10mL丙酮:正己烷(1:1),超声波萃取30min。硅胶柱净化,用30mL正己烷洗脱。样品浓缩后,用正己烷定容至10mL,进行GCMS分析。

分析结果

图1为16种0.1 μg/mL PAHs的MIC, 峰顶标有数字的谱图为TIC, 每种化合物选择一个特征离子作MC。图2表明16种0.1 μg/mL PAHs由Scan方式得到的质谱图和与之相对应的NIST05标准质谱图比较。表1为16种PAHs九个浓度点的线性方程, 浓度设置分别为0.001, 0.005, 0.01, 0.05, 0.1, 0.3, 0.5, 1.0, 5.0 μg/mL。表2是0.1 μg/mL PAHs添加到样品中,经过样品处理后测得的回收率和重现性。图3是未知橡胶样品的MIC图。橡胶样品中PAHs的含量测定结果如表4所示。

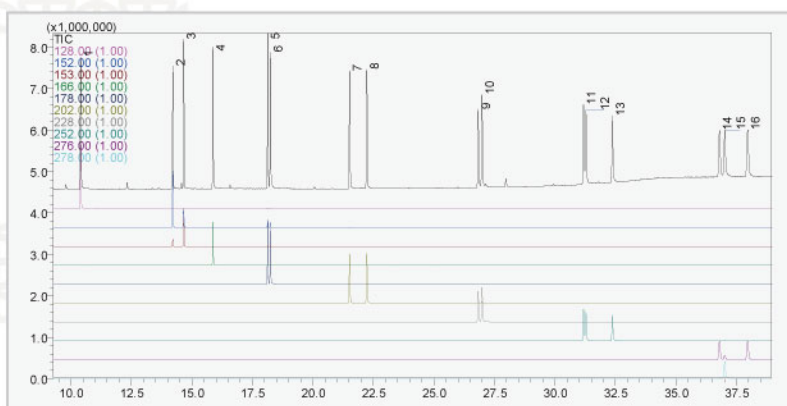
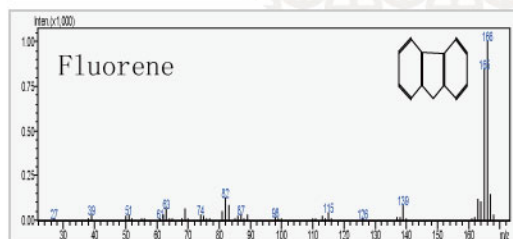
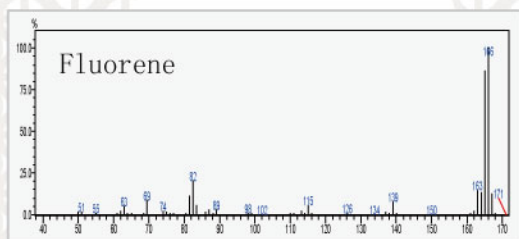
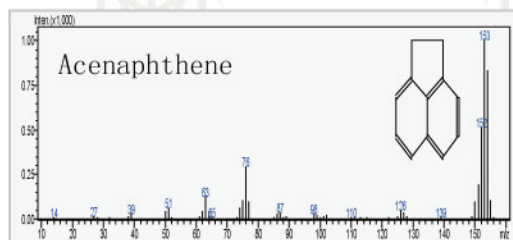
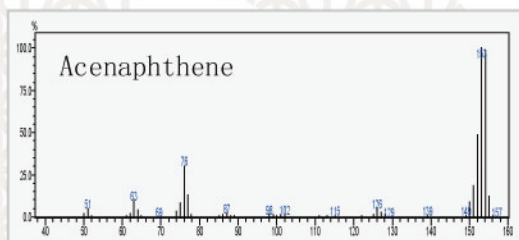
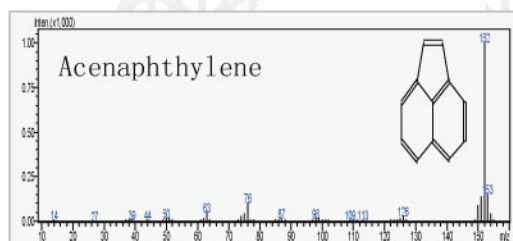
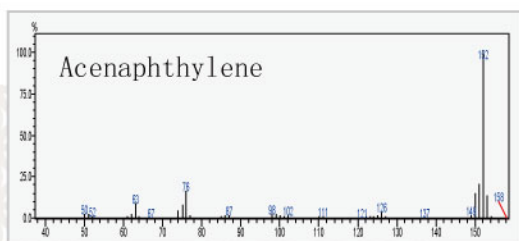
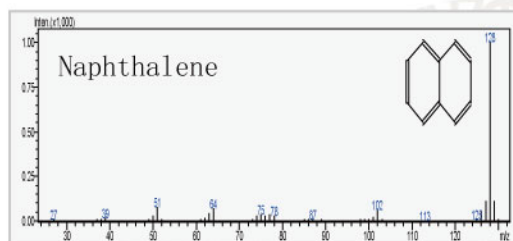
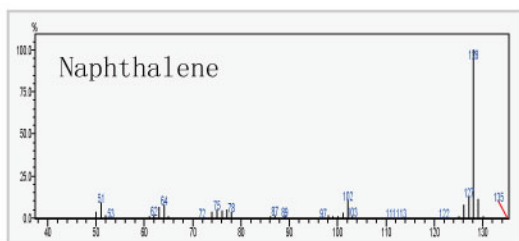


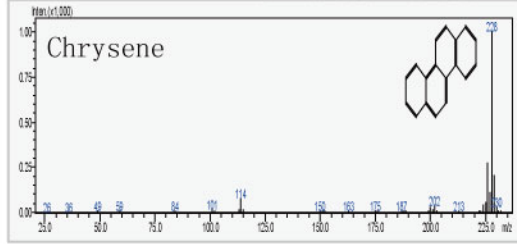
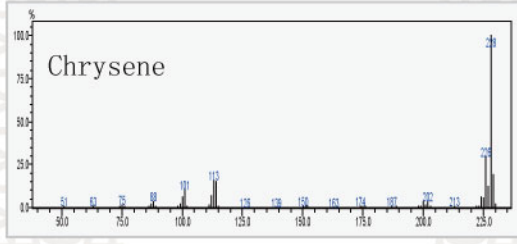
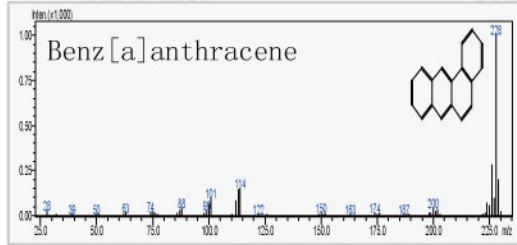
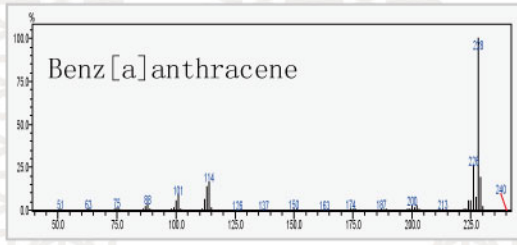
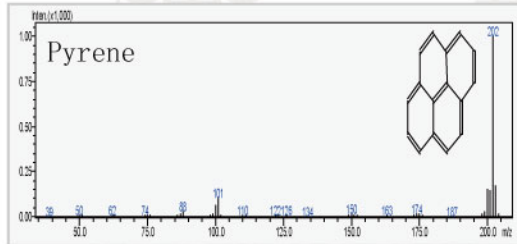
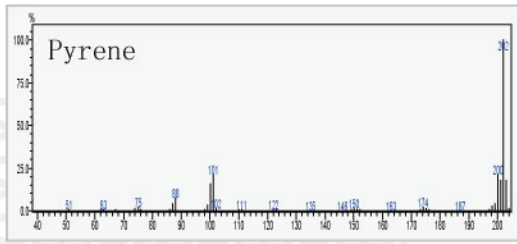
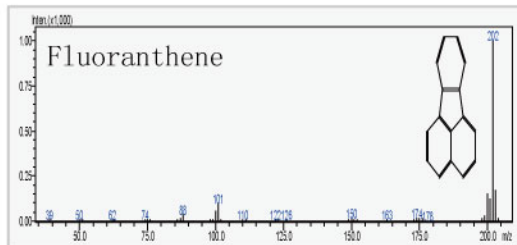
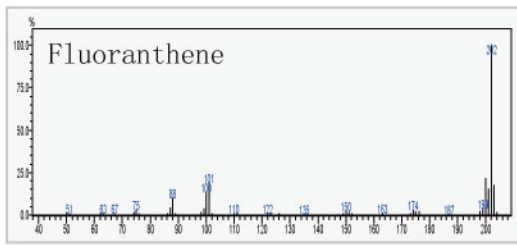
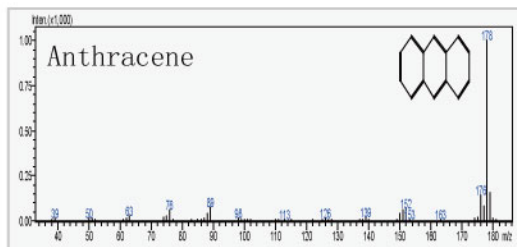
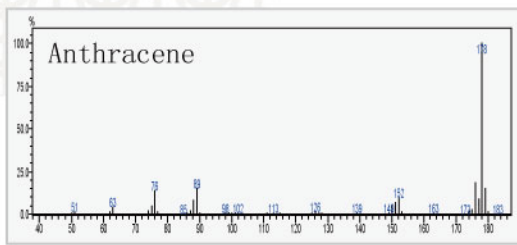
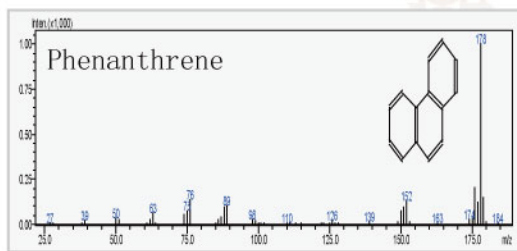
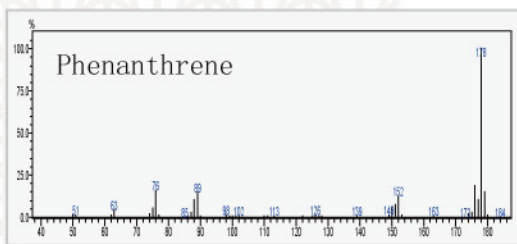
图1 Scan方式采集的0.1 μg/mL 16种PAHs的MIC

图2 Scan方式采集到的质谱图和标准质谱图比较

Scan方式采集的质谱图

NIST05标准质谱图





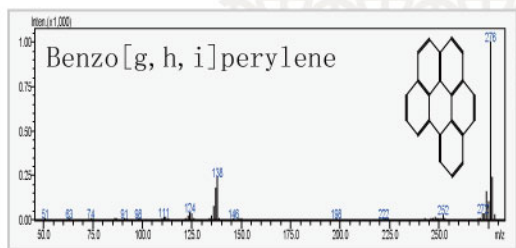
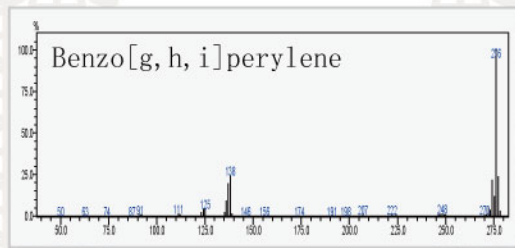
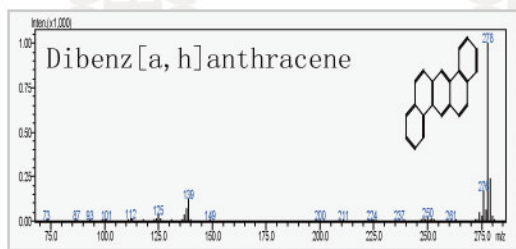
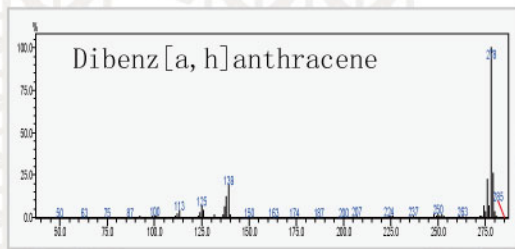
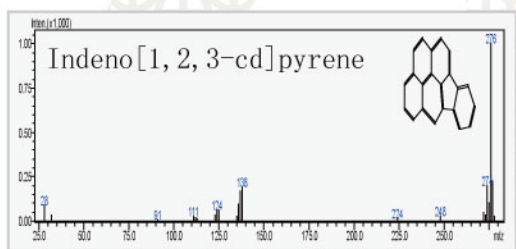
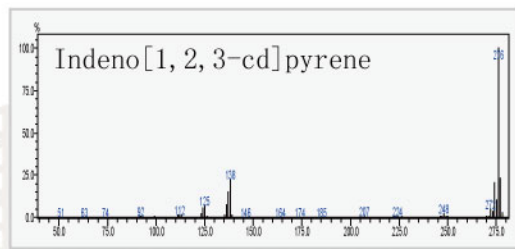
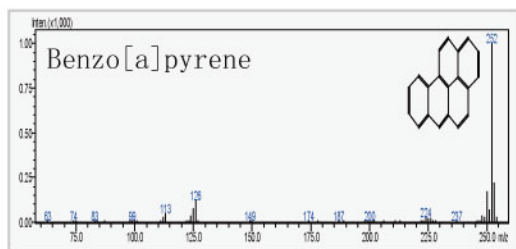
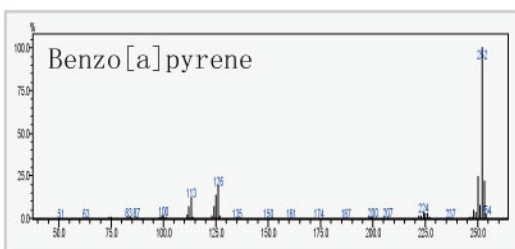
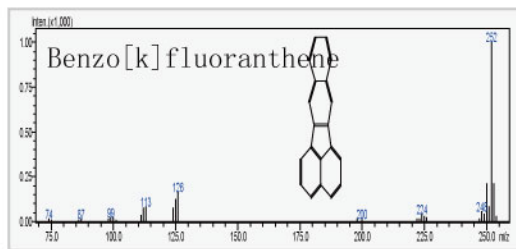
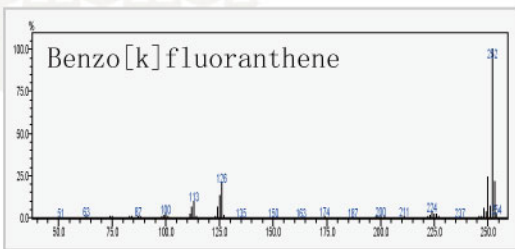
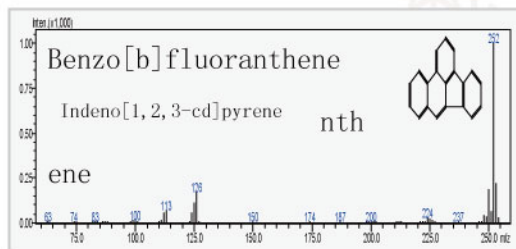
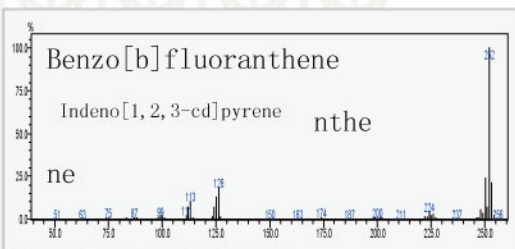


表1 16种PAHs的线性方程

| 编号 | 化合物名称 | 线性方程 | 线性相关系数 |
|----|------------------------|----------------------------|----------|
| 1 | Naphthalene | $Y = 1568586X + 14692.18$ | 0.999939 |
| 2 | Acenaphthylene | $Y = 1540088X - 29138.69$ | 0.999888 |
| 3 | Acenaphthene | $Y = 996357.8X + 4335.094$ | 0.999954 |
| 4 | Fluorene | $Y = 1133960X - 14896.49$ | 0.999953 |
| 5 | Phenanthrene | $Y = 1665056X - 25738.44$ | 0.999939 |
| 6 | Anthracene | $Y = 1697882X - 32732.46$ | 0.999891 |
| 7 | Fluoranthene | $Y = 2040280X - 55994.86$ | 0.99979 |
| 8 | Pyrene | $Y = 2170708X - 62437.67$ | 0.999745 |
| 9 | Benz[a]anthracene | $Y = 1957560X - 120554.1$ | 0.999833 |
| 10 | Chrysene | $Y = 2081206X - 53691.55$ | 0.999765 |
| 11 | Benzo[b]fluoranthene | $Y = 2114751X - 114710.6$ | 0.999979 |
| 12 | Benzo[k]fluoranthene | $Y = 2179265X - 73142.47$ | 0.999532 |
| 13 | Benzo[a]pyrene | $Y = 2048676X - 126888.0$ | 0.999706 |
| 14 | Indeno[1,2,3-cd]pyrene | $Y = 2051834X - 136946.3$ | 0.999055 |
| 15 | Dibenz[a,h]anthracene | $Y = 1994199X - 120554.9$ | 0.999428 |
| 16 | Benzo[g,h,i]perylene | $Y = 2114283X - 91927.9$ | 0.999112 |

表2 16种0.1ppm PAHs的添加回收率

| 名称 | 保留时间 (min) | 定量离子 (m/z) | 回收率 (%) | RSD (%) |
|------------------------|-----------------|-----------------|--------------|--------------|
| Naphthalene | 10.392 | 128 | 85.17 | 2.584505 |
| Acenaphthylene | 14.2 | 152 | 93.53 | 2.151306 |
| Acenaphthene | 14.65 | 153 | 104.8 | 3.022132 |
| Fluorene | 15.86 | 166 | 114.61 | 2.015553 |
| Phenanthrene | 18.126 | 178 | 116.31 | 2.985899 |
| Anthracene | 18.232 | 178 | 111.49 | 2.370048 |
| Fluoranthene | 21.503 | 202 | 102.16 | 2.823175 |
| Pyrene | 22.211 | 202 | 98.38 | 2.429405 |
| Benz[a]anthracene | 26.818 | 228 | 118.99 | 2.396417 |
| Chrysene | 26.982 | 228 | 101.16 | 2.797649 |
| Benzo[b]fluoranthene | 31.307 | 252 | 110.25 | 2.364264 |
| Benzo[k]fluoranthene | 31.395 | 252 | 100.09 | 2.352687 |
| Benzo[a]pyrene | 32.45 | 252 | 101.02 | 1.192181 |
| Indeno[1,2,3-cd]pyrene | 36.799 | 276 | 113.44 | 1.313511 |
| Dibenz[a,h]anthracene | 37.011 | 278 | 81.11 | 2.115278 |
| Benzo[g,h,i]perylene | 37.964 | 276 | 98.89 | 1.957942 |

图3 Scan方式采集的橡胶样品的MIC

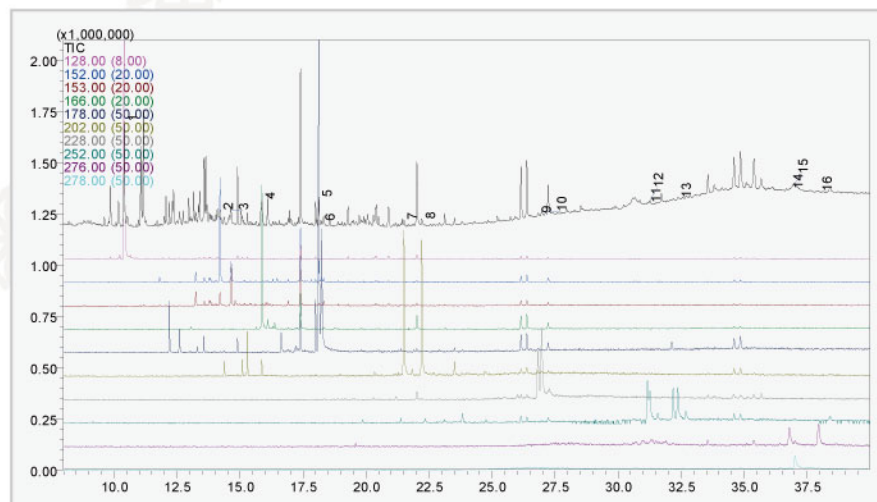


表3 橡胶样品中PAHs测定结果

| 编号 | 名称 | 浓度($\mu\text{g/ml}$) | 保留时间(min) | 定量离子(m/z) | RSD(%) |
|----|------------------------|------------------------|-----------|-----------|----------|
| 1 | Naphthalene | 4.1955 | 10.399 | 128 | 1.726223 |
| 2 | Acenaphthylene | 0.60116 | 14.2 | 152 | 1.447774 |
| 3 | Acenaphthene | 0.20121 | 14.648 | 153 | 2.621353 |
| 4 | Fluorene | 0.88975 | 15.86 | 166 | 2.535466 |
| 5 | Phenanthrene | 1.1817 | 18.122 | 178 | 2.497894 |
| 6 | Anthracene | 0.50844 | 18.231 | 178 | 2.011785 |
| 7 | Fluoranthene | 0.6846 | 21.498 | 202 | 2.130195 |
| 8 | Pyrene | 0.65812 | 22.205 | 202 | 2.091782 |
| 9 | Benz[a]anthracene | 0.88472 | 26.813 | 228 | 1.187043 |
| 10 | Chrysene | 0.69238 | 26.961 | 228 | 1.326832 |
| 11 | Benzo[b]fluoranthene | 0.71376 | 31.162 | 252 | 1.354032 |
| 12 | Benzo[k]fluoranthene | 0.48632 | 31.255 | 252 | 1.977726 |
| 13 | Benzo[a]pyrene | 0.7762 | 32.354 | 252 | 2.287926 |
| 14 | Indeno[1,2,3-cd]pyrene | 0.75397 | 36.783 | 276 | 2.653644 |
| 15 | Dibenz[a,h]anthracene | 0.65709 | 36.992 | 278 | 1.116197 |
| 16 | Benzo[g,h,i]perylene | 0.55971 | 37.927 | 276 | 2.196357 |

结论

EPA相关16种多环芳烃的MIC以及和标准质谱图的比较表明, GCMS QP-2010 Plus分析该类化合物可以得到非常好的分离度、灵敏度及其与标准质谱图的相似性。16种PAHs浓度从1.0ng/mL至5.0 $\mu\text{g/mL}$ 做线性方程, 线性相关系数都在0.999以上。参照EPA8270的方法对PVC和橡胶样品处理后用GCMS测定, 测得的样品浓度重现性比较好, 16种PAHs的回收率都在80%至120%之间。