## Supplemental Information for

## Universal Microfluidic Automaton for Autonomous Sample Processing: Application to the Mars Organic Analyzer

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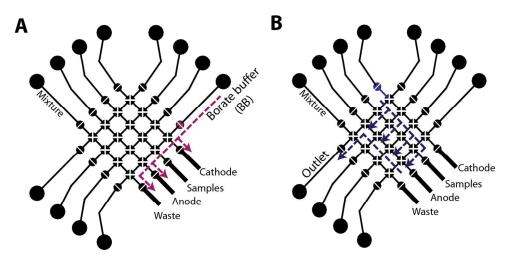
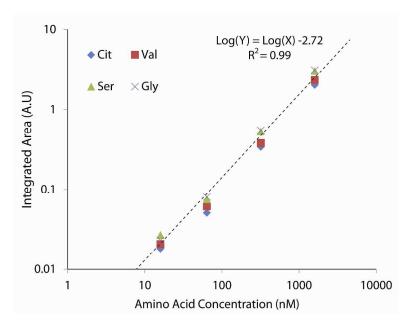


Figure SI1. Detail of (A) buffer loading process and (B) washing process.



**Figure SI2**. Integrated peak area as a function of 4 different amino acid concentrations resulting from the automated sample processing program. There is a log-linear correlation between concentration and integrated area as expected.

**Table SI1-1.** Off-chip vs. on-chip labeling and separation of an amino acid standard.

|            | Labeling           | Efficiency         | Separation Efficiency<br>(Peak Efficiency, Theoretical Plates) |                     |  |
|------------|--------------------|--------------------|--|---------------------|--|
|            | (Peak Area, Rel. F | luorescence Units) |  |                     |  |
|            | Off-Chip Manual    | On-Chip            | Off-Chip   | On-Chip Autonomous  |  |
|            | On-Chip Manual     | Autonomous         | Manual   | On-Chip Autonomous  |  |
| Cit        | 0.44               | 0.53               | $2.9 \times 10^{5}$  | 2.5×10 <sup>5</sup> |  |
| Val        | 0.46               | 0.57               | $2.8 \times 10^{5}$  | $2.4 \times 10^{5}$ |  |
| Ser        | 0.55               | 0.74               | $2.7 \times 10^{5}$  | $2.2 \times 10^{5}$ |  |
| Ala        | 0.21               | 0.28               | $2.7 \times 10^{5}$  | $2.2 \times 10^{5}$ |  |
| Gly        | 0.70               | 0.95               | $2.4 \times 10^{5}$  | $2.2 \times 10^{5}$ |  |
| Glu        | 0.41               | 0.61               | $1.8 \times 10^{5}$  | $1.5 \times 10^{5}$ |  |
| Asp        | 0.23               | 0.31               | $1.8 \times 10^{5}$  | $1.7 \times 10^{5}$ |  |
| Average    | 0.43               | 0.57               | $2.5 \times 10^{5}$  | $2.1 \times 10^{5}$ |  |
| Normalized | 1.0                | 1.3                | 1.0  | 0.9                 |  |

Table SI1-2. Off-chip vs. on-chip labeling and separation of an aldehyde and ketone standard.

|                    | · · · · · · · · · · · · · · · · · · · | g Efficiency<br>Fluorescence Units) | Separation Efficiency<br>(Peak Efficiency, Theoretical<br>Plates) |                     |  |
|--------------------|---------------------------------------|-------------------------------------|---|---------------------|--|
|                    | Off-Chip                              | On-Chip                             | Off-Chip  | On-Chip             |  |
|                    | Manual                                | Autonomous                          | Manual  | Autonomous          |  |
| Methylethyl ketone | 0.25                                  | 0.17                                | $3.5 \times 10^{5}$   | 3.6×10 <sup>5</sup> |  |
| Propionaldehyde    | 1.9                                   | 1.3                                 | $3.1 \times 10^{5}$   | $3.3 \times 10^{5}$ |  |
| Acetaldehyde (1)   | 1.7                                   | 1.2                                 | $2.9 \times 10^{5}$   | $3.2 \times 10^{5}$ |  |
| Acetaldehyde (2)   | 0.21                                  | 0.14                                | $2.5 \times 10^{5}$   | $2.8 \times 10^{5}$ |  |
| Formaldehyde       | 1.7                                   | 1.2                                 | $4.0 \times 10^{5}$   | $3.3 \times 10^{5}$ |  |
| Average            | 1.1                                   | 0.82                                | $3.2 \times 10^{5}$   | $3.2 \times 10^{5}$ |  |
| Normalized         | 1.0                                   | 0.8                                 | 1.0   | 1.0                 |  |

**Table SI1-3.** Off-chip vs. on-chip labeling and separation of a carboxylic acid standard.

|                | Labelin          | g Efficiency        | Separation Efficiency                 |                     |  |  |
|----------------|------------------|---------------------|---------------------------------------|---------------------|--|--|
|                | (Peak Area, Rel. | Fluorescence Units) | (Peak Efficiency, Theoretical Plates) |                     |  |  |
|                | Off-Chip         | On-Chip             | Off-Chip                              | On-Chip             |  |  |
|                | Manual           | Autonomous          | Manual                                | Autonomous          |  |  |
| Valeric acid   | 0.28             | 0.33                | $0.6 \times 10^{5}$                   | $0.5 \times 10^5$   |  |  |
| Butanoic acid  | 0.32             | 0.42                | $1.0 \times 10^{5}$                   | $0.8 \times 10^{5}$ |  |  |
| Propionic acid | 0.66             | 0.87                | $2.1 \times 10^{5}$                   | $1.2 \times 10^{5}$ |  |  |
| Acetic acid    | 0.37             | 0.54                | $1.0 \times 10^{5}$                   | $0.8 \times 10^{5}$ |  |  |
| Formic acid    | 0.63             | 1.0                 | $0.9 \times 10^{5}$                   | $0.8 \times 10^{5}$ |  |  |
| Average        | 0.45             | 0.64                | $1.1 \times 10^{5}$                   | $0.8 \times 10^{5}$ |  |  |
| Normalized     | 1.0              | 1.4                 | 1.0                                   | 0.7                 |  |  |

**Table SI02.** Separation characteristics from figure 5E

|                              | Total An    | Total Analysis      |                     |                         | Amino Acid Analysis |                         | Aldehyde / Ketone Analysis |                         | Carboxylic Acid<br>Analysis |                         |
|------------------------------|-------------|---------------------|---------------------|-------------------------|---------------------|-------------------------|----------------------------|-------------------------|-----------------------------|-------------------------|
| Species                      | Conc.       | Signal-<br>to-Noise | $N^a$               | Resolution <sup>b</sup> | $N^a$               | Resolution <sup>b</sup> | $N^a$                      | Resolution <sup>b</sup> | $N^a$                       | Resolution <sup>b</sup> |
| Cit                          | 400 nM      | 1200                | 3.6×10 <sup>5</sup> |                         | $3.7 \times 10^5$   |                         |                            |                         |                             |                         |
| Val                          | 400 nM      | 1300                | $3.4 \times 10^{5}$ | 7.7                     | $3.6 \times 10^5$   | 7.9                     |                            |                         |                             |                         |
| Ser                          | 400 nM      | 1200                | $3.2 \times 10^{5}$ | 6.0                     | $3.3 \times 10^5$   | 6.1                     |                            |                         |                             |                         |
| Gly                          | 400 nM      | 1500                | $2.9 \times 10^{5}$ | 7.8                     | $3.0 \times 10^{5}$ | 8.0                     |                            |                         |                             |                         |
| Acetone                      | 400 nM      | 4000                | $2.9 \times 10^{5}$ | 15                      |                     |                         | $3.0 \times 10^{5}$        |                         |                             |                         |
| PB (1)                       |             | 900                 | $2.8 \times 10^{5}$ | 0.66                    | $2.6 \times 10^{5}$ | 16                      |                            |                         |                             |                         |
| Acetic acid                  | 400 nM      | 2800                | $1.3 \times 10^{5}$ | 3.3                     |                     |                         |                            |                         | $1.3 \times 10^5$           |                         |
| PB (2)                       |             | 1200                | $2.8 \times 10^{5}$ | 0.96                    | $3.2 \times 10^{5}$ | 5.4                     |                            |                         |                             |                         |
| Formaldehyde                 | 40 nM       | 4100                | $2.8 \times 10^{5}$ | 5.3                     |                     |                         | $2.7 \times 10^{5}$        | 11                      |                             |                         |
| СВ                           |             | $NA^c$              | $NA^c$              | 4.2                     |                     |                         | $NA^c$                     | $4.4^d$                 | $NA^c$                      | $9.6^{d}$               |
| Formic acid                  | 40 nM       | 4100                | $1.0 \times 10^{5}$ | $4.2^{d}$               |                     |                         |                            |                         | $1.1 \times 10^5$           | $5.2^{d}$               |
| <sup>a</sup> Peak efficiency | (theoretica | al plates).         |                     |                         | •                   |                         | •                          |                         | •                           |                         |
| <sup>b</sup> Resolution bety |             |                     | and the previ       | ously eluting pea       | ak in the sepa      | ration.                 |                            |                         |                             |                         |
| <sup>c</sup> Cannot be quan  |             |                     |                     |                         |                     |                         |                            |                         |                             |                         |
| <sup>d</sup> Estimated.      |             | 1                   | S                   |                         |                     |                         |                            |                         |                             |                         |