Electronic Supplementary Material (ESI) for Analytical Methods.

ICP-MS DNA Assay based on Lanthanide Labels and Hybridization Chain Reaction Amplification

Chong Deng, Chong-Hua Zhang, Hao Tang* and Jian-Hui Jiang

State Key Laboratory for Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha, 410082, P. R. China.

Table S1. Sequences of oligonucleotide probes used in this work[a]

Capture DNA Probe 1(C1)	5 ’-**TGTACTGAGCAATCTGGAAGCGACG**TTTTTT-3’biotin
Target (Thymidine Kinase 1mRNA)	5’-**CGTCGCTTCCAGATTGCTCAGTACA*AGTGCCTGGTGATCAAGTA TGCCAA***-3’
Capture DNA Probe 2(C2)	5’-AGTCTAGGATTCGGCGTGGGTTAA***TTGGCATACTTGATCACCAGGCAC T***-3’
H1	5’-TTAACCCACGCCGAATCCTAGACTCAAAGTAGTCTAGGATTCGGC GTG-3’
H2	5’-SH-AGTCTAGGATTCGGCGTGGGTTAACACGCCGAATCCTAGACTACTTTG -3’
S1	5’-CGTGTGCACATCGCTCAGTACACGTGCTCGTGCTGGTA TGGCCA-3’
S2	5’-GGCTGTACTGGAACAGACTCTTTTGTTCCAGTACAGCCAGGCTGTACT GGA-3’

[a]The underline section in C2 is the initiation sequence for HCR. Bold font in C1 and target DNA are complementary sequences. Italics bold font in C2 and target are complementary sequences.

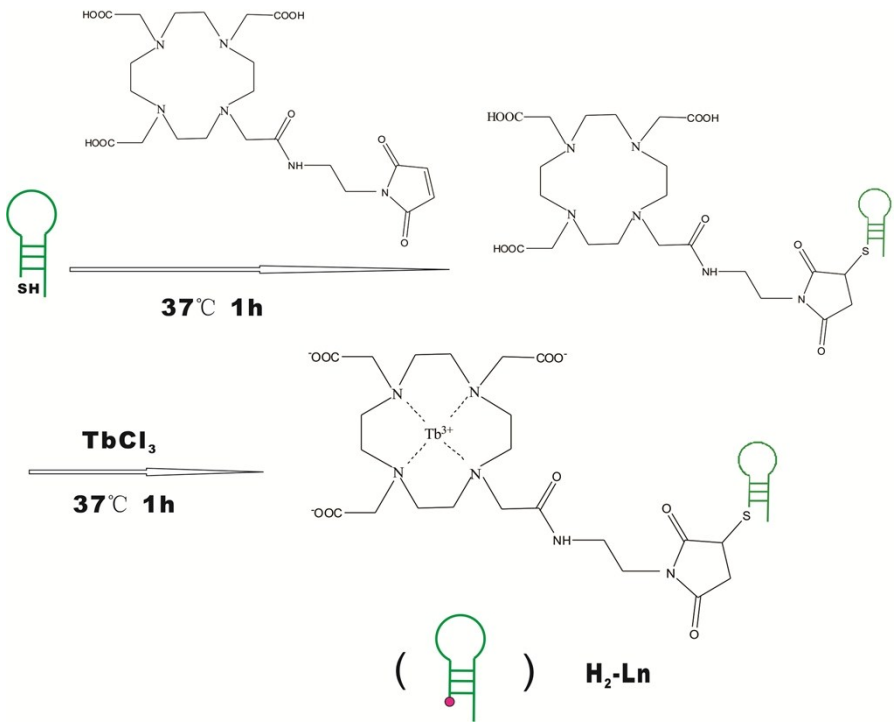

Figure S1. Process of labeling DNA with lanthanide elemental tag. The oligonucleotide with an -SH group was conjugated with MMA-DOTA, and then lanthanide was chelated in the macrocycle DOTA.

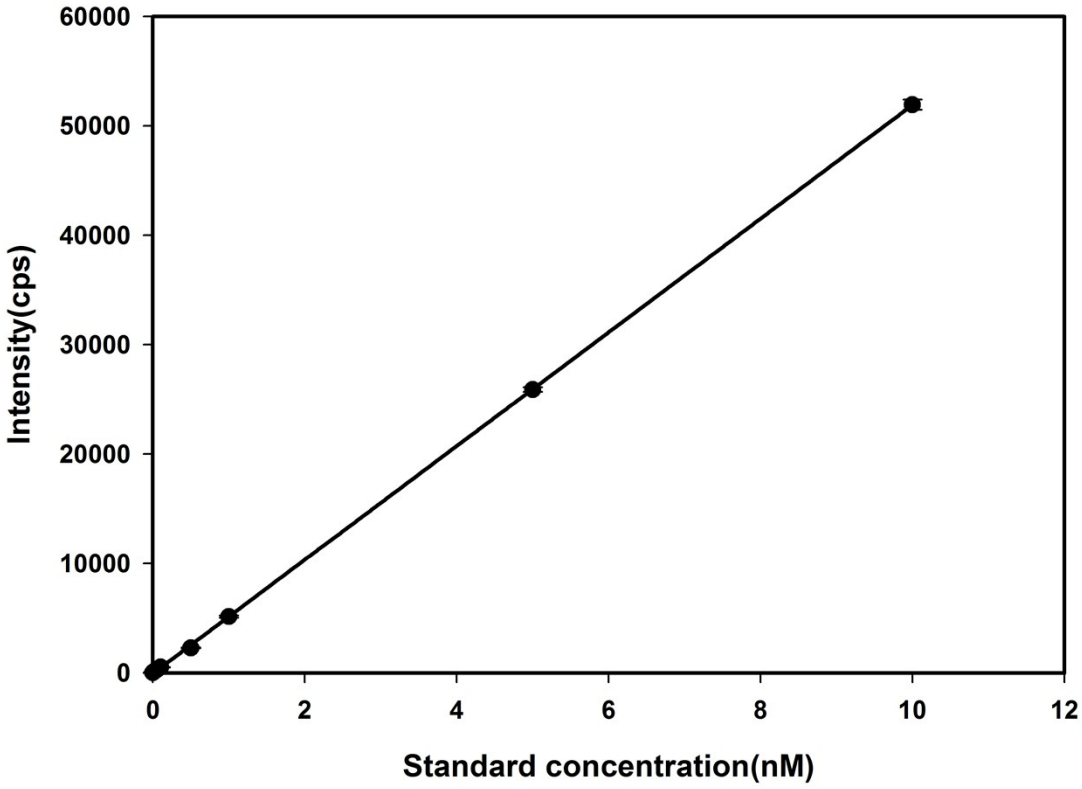

Figure S2. ICP-MS signals to different concentrations (10 pM, 50 pM, 100 pM, 1 nM, 5 nM and 10 nM) of $TbCl_3$ solution. The linear equation is y= -50.81+5195.2*x, R^2=0.99.

Table S2. The parameters for ICP-MS.

Nebulizer Gas Flow	0.9L/min
Auxliary Gas Flow	1.2L/min
Plasma Gas Flow	15L/min
ICP RF Power	1100W
Pulse stage Voltage	800V
Dwell time	50ms
Isotope monitored0.9	^{159}Tb

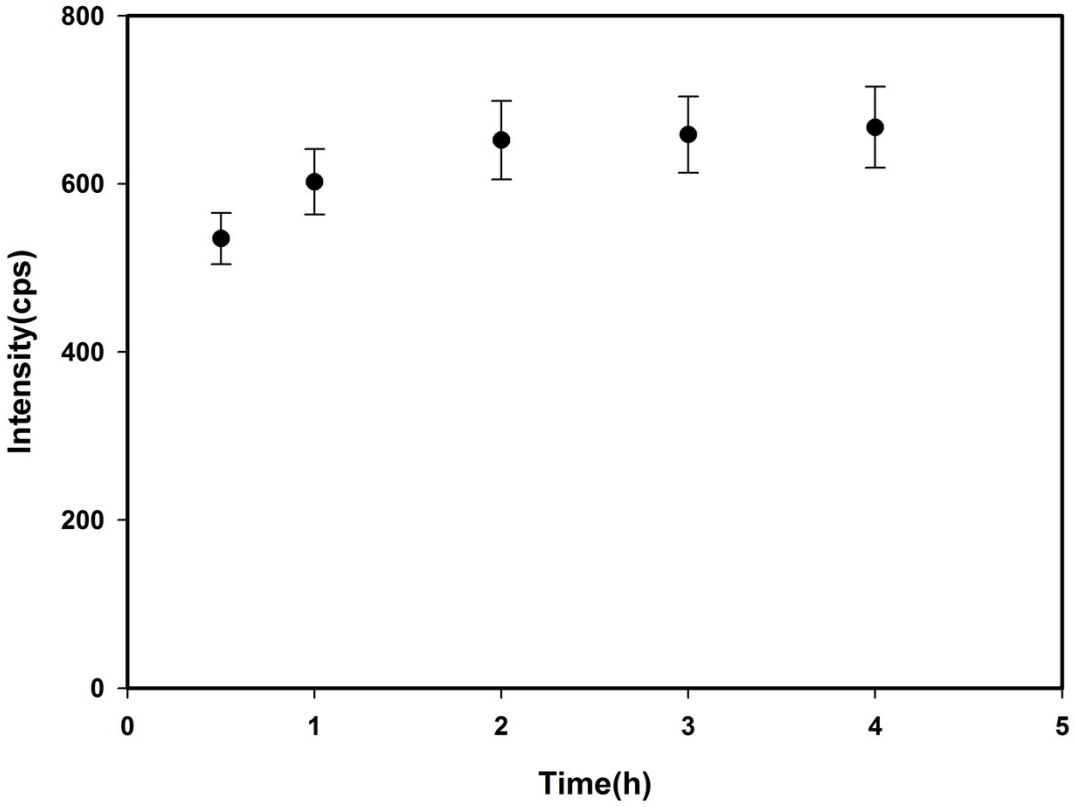

Figure S3. The ICP-MS signal intensity for DNA samples using different HCR reaction time. The sample DNA concentration is 500 pM and the HCR based assay process is the same as described in section 2.4.

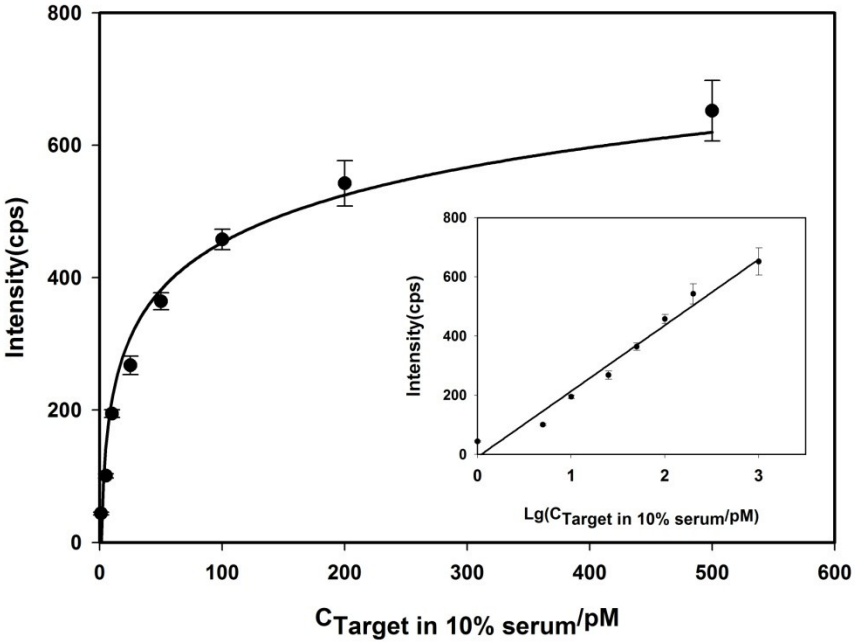

Figure S4. ICP-MS signals in response to TK1 mRNA of various concentrations in 10% bovine serum. Inset: linear relationship between the intensity and the logarithm of target DNA concentration. Error bars are standard deviation of three repetitive experiments.

Table S3 . Recovery experiments of TK1 mRNA in 10% human sera samples

Samples	Added TK1 mRNA (pM)	Detected TK1 mRNA [a] (pM)	Recovery (%)
1	0	2.21±0.15	
2	10	9.12±1.22	91.2
3	100	93.67±6.21	93.7
4	200	196.37 ±2.31	98.2
5	500	523.24 ±5. 30	104.5

[a]Average of three determinations ± standard deviation