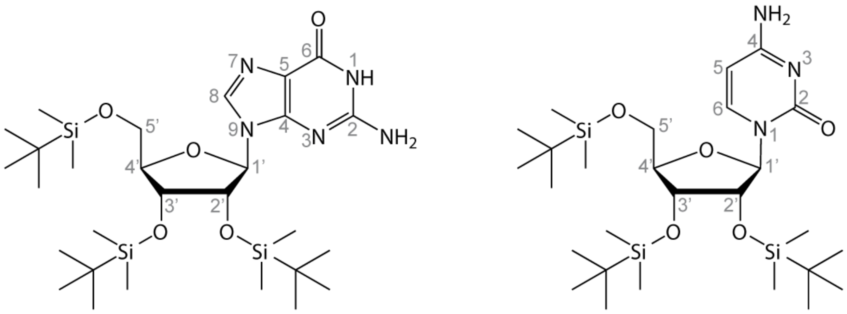
Electronic Supplementary Information


2’,3’,5’-O-tris(tert-butyldimethylsilyl)guanosine 2’,3’,5’-O-tris(tert-butyldimethylsilyl)cytidine

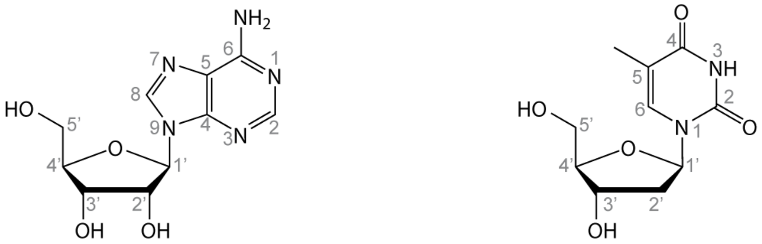

adenosine thymidine

Figure S1: Structures of the monomers used: 2´,3´,5´-O-tris(tert-butyldimethylsilyl)guanosine, 2´,3´,5´-O-tris(tert-butyldimethylsilyl)cytidine, adenosine and thymidine.

Synthesis

The guanosine and cytidine derivatives were synthesized according to Sheu and Ogilvie [42, 43]. For preparation of 2´,3´,5´-O-tris(tert-butyldimethylsilyl)guanosine 2.025 g guanosine (SIGMA, 98%), 4.817 g imidazole and 4.255 g TBDMSCl (tert-butyldimethylsilylchloride) were dissolved under nitrogen in 30 ml dry DMF (dimethylformamide). The solution was stirred for 24 h at room temperature. Afterwards 20 ml water and 20 ml ethyl acetate were added. The aqueous phase was washed three times with 20 ml ethyl acetate and the joined organic phases were dried over MgSO4. After filtration the solution was reduced under vacuum to yellow oil. The product was precipitated as a white solid by addition of 20 ml water and dried under vacuum. For preparation of 2´,3´,5´-O-tris(tert-butyldimethylsilyl)cytidine 1.787 g cytidine (SIGMA, 98%) were used. The synthesis was performed as described for 2´,3´,5´-O-tris(tertbutyldimethylsilyl)-guanosine. All samples were characterized by NMR spectroscopy and mass spectrometry.
2´,3´,5´-O-Tris(tert-butyldimethylsilyl)guanosine:
1H-NMR (500 MHz, DMSO-d6): δ = -0.18 (s, 6H, Si(CH3)2), -0.01 (s, 6H, Si(CH3)2), 0.00 (s, 6H, Si(CH3)2), 0.81 (2s, 27H, SiC(CH3)3), 3.60 – 3.77 (m, 2H, 5´-H), 3.85 (m, 1H, 4´-H), 4.07 (m, 1H, 2´-H), 4.49 (m, 1H, 3´-H), 6.36 (s, 1H, 1´-H), 6.91 (s, 2H, NH2), 7.79 (s, 1H, 1-H), 10.52 (s, 1H, NH) ppm.
13C-NMR (125 MHz, DMSO-d6): δ = -5.14, -5.10, -5.09, -4.44, -4.40,-4.30 (Si(CH3)2), 17.93, 18.17, 18.39 (SiC(CH3)), 25.83, 26.10, 26.21 (SiC(CH3)3), 63.34 (5´-C), 73.30 (3´-C), 75.58 (2´-C), 85.39 (1´-C), 86.11 (4´-C), 116.69 (2-C), 135.47 (1-C), 151.98 (5-C), 154.25 (4-C), 157.09 (3-C) ppm.
ESI: m/z : 626 [M]+, 649 (+Na+), 511 (-Si(CH3)2C(CH3)3)
2´,3´,5´-O-tris(tert-butyldimethylsilyl)cytidine:
1H-NMR (300 MHz, CDCl3): δ = -0.07 (2s, every 3H, Si(CH3)2), -0.01-0.00 (2s, every 3H, Si(CH3)2), 0.02 (s, 3H, Si(CH3)2), 0.11 (s, 3H, Si(CH3)2), 0.77 (s, 9H, SiC(CH3)3), 0.79 (s, 9H, SiC(CH3)3), 0.84 (s, 9H, SiC(CH3)3), 1.59 (s, 2H, NH2), 3.66 (dd, 1H, 2’-H), 3.89-4.00 (m, 4H, 5’-H, 4’-H, 3’-H), 5.46 (d, 1H, 3-H), 5.67 (d, 1H, 1’-H), 8.07 (d, 1H, 4-H) ppm.
13C-NMR (75 MHz, CDCl3): δ = -5.54, -5.28, -5.11, -5.02, -4.12, -4.08 (Si(CH3)2), 18.06, 18.09, 18.55 (SiC(CH3)), 25.88, 25.92, 26.10 (SiC(CH3)3), 60.89 (5’-C), 69.22 (3’-C), 76.25 (2’-C), 82.82 (1’-C), 90.37 (4’-C), 92.95 (3-C), 142.06 (4-C), 155.74 (1-C), 165.51 (2-C) ppm.
ESI: m/z : 585.5 [M]+, 609 (+Na+).
Adenosine (Acros Organics, >99%) and thymidine (Sigma Aldrich, >99%) were used without further purification.

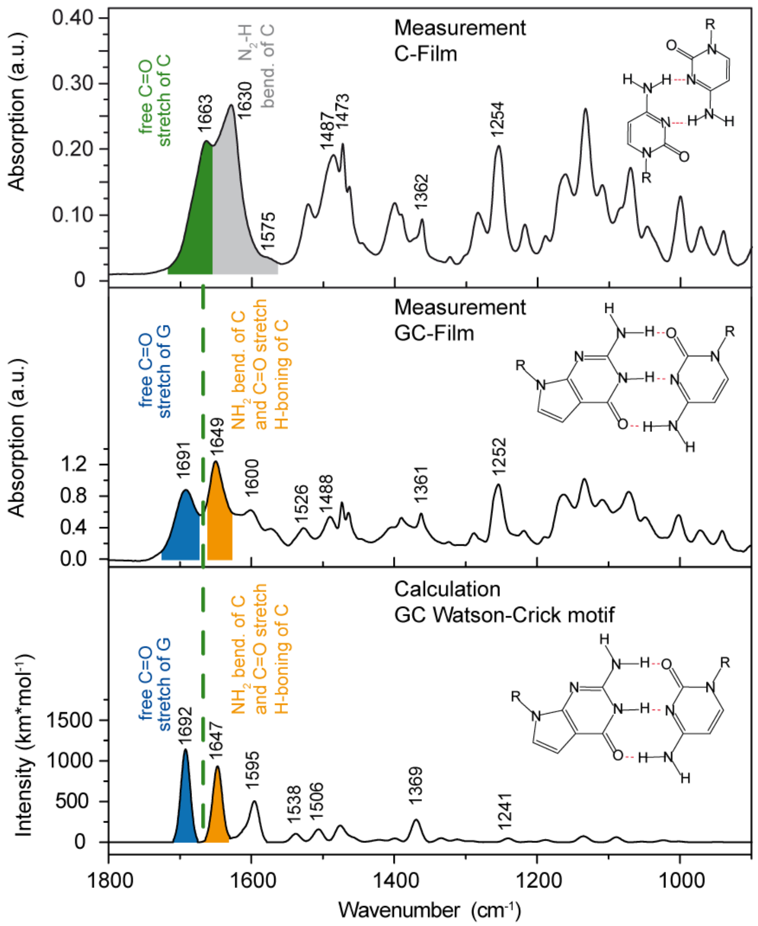


Figure S2: Comparison of the IR Absorption spectra before irradiation of a C film, a mixed GC film and a calculated spectrum (DFT/TZVP/B3LYP) of the GC Watson Crick base pair. The free C=O stretch vibration in the C film is observed at 1663 cm^{-1}. The proposed dimer structure is shown as inset. In the mixed GC film only the combined H-bonded C=O stretch vibration an NH_2 vibration of C at 1649 cm^{-1} is observed. The calculated structure is shown as inset. The calculation is scaled with 0.957.

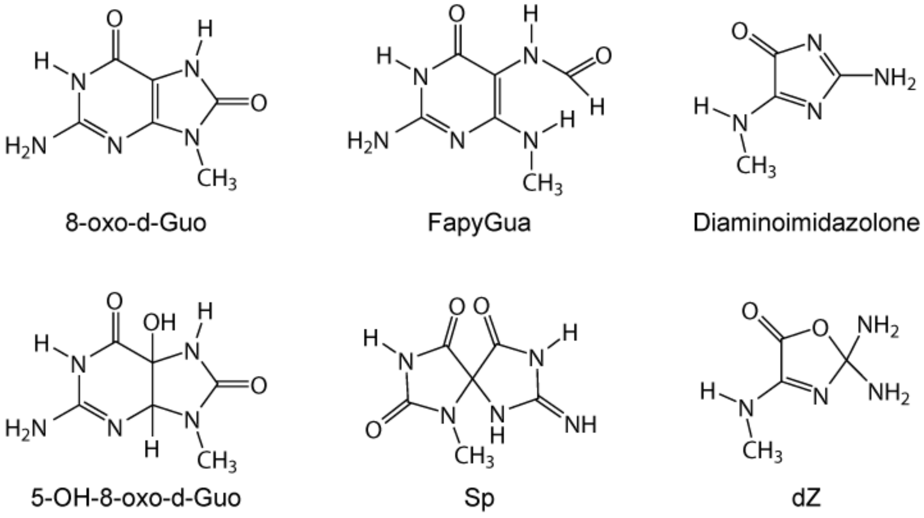


Figure S3: Structures of the calculated oxidation products or hydrates of G. We compared the experimental broad spectra with calculated spectra of several possible oxidation products or hydrates discussed in the literature, like the 8-oxo-7,8-dihydro-2’-deoxyguanosine (short: 8-oxo-d-Guo), the 5-OH-8-oxoGuo, a spiroiminodihydantoin nucleoside (Sp), the 2,6-diamino-4-hydroxy-5-formamidopyrimidine (FapyGua), the 2,2,4,-triamino-5(2H)-oxazolone (dZ) and the 2,5-diamino-4H-imidazol-4-one (Diaminoimidazolone) [15, 32]. The comparison does not point to any of these products in our experiment, which was performed in vacuum in the absence of oxygen and water.

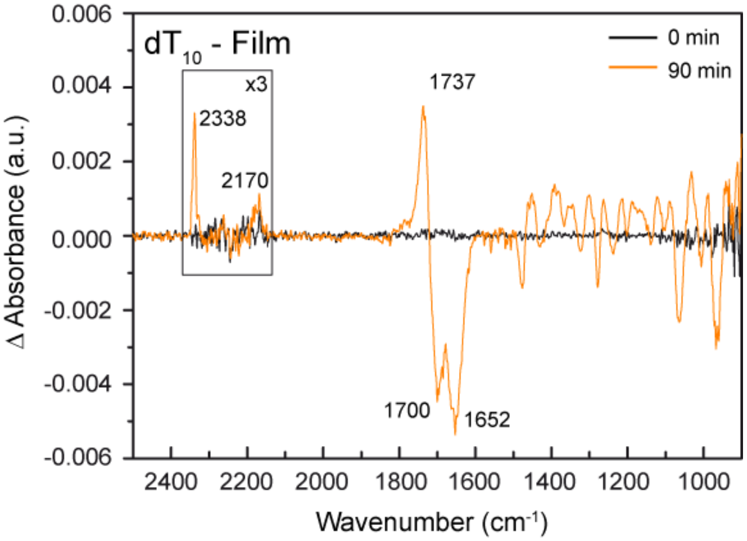


Figure S4: Isocyanate formation in dT_{10} upon irradiation with a UV lamp. The spectral region between 2100 cm^{-1} and 2400 cm^{-1} is enlarged by a factor of 3.

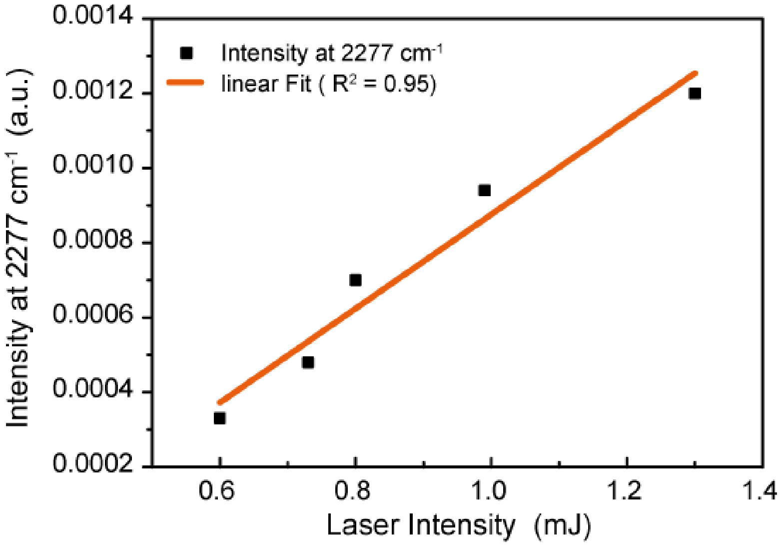


Figure S5: IR Absorption at 2277 cm^{-1} after 10 minutes dependence on the laser intensity and the corresponding linear fit.

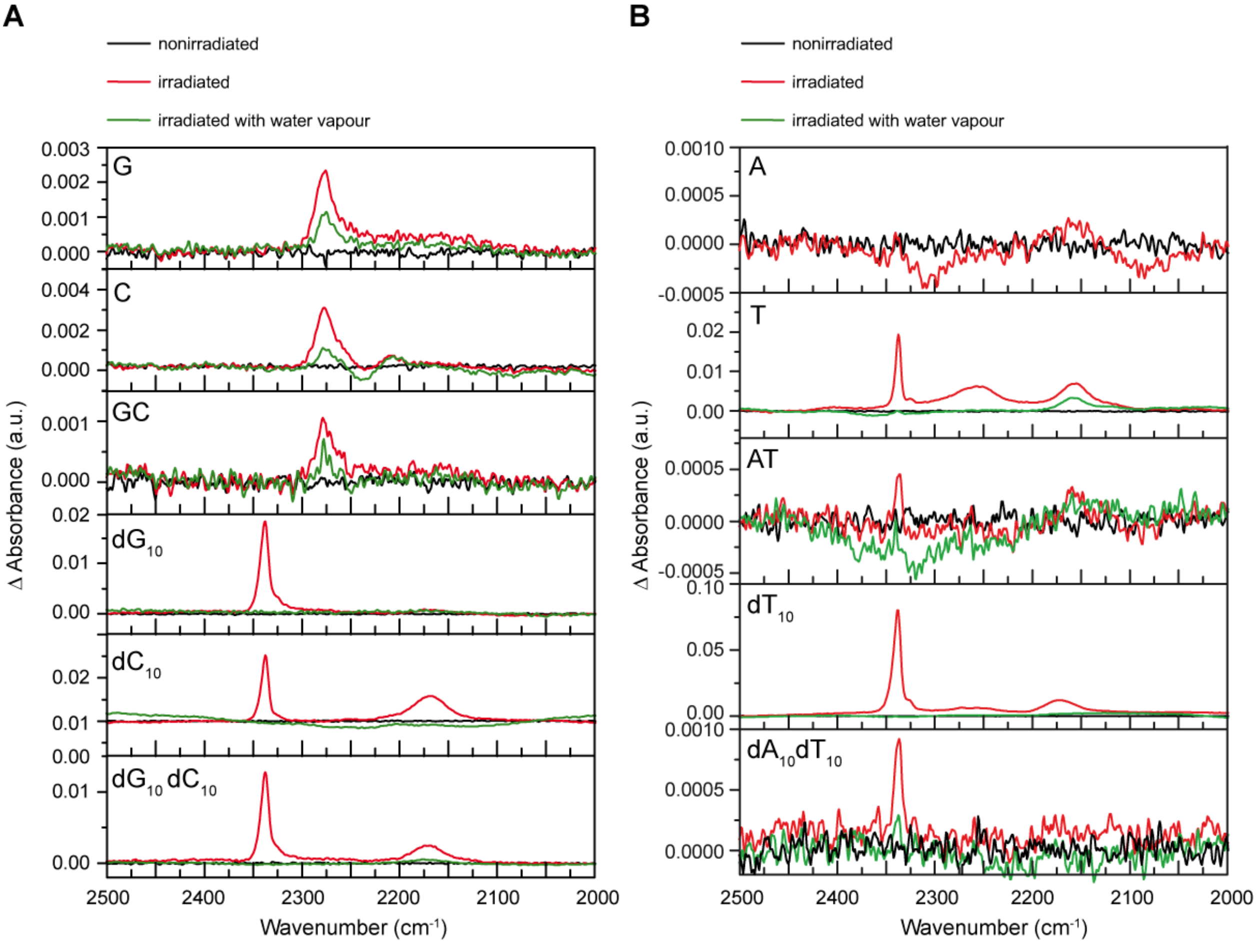


Figure S6: A: Reaction of isocyanate photo-products with water vapour. The isocyanate band at 2277 cm^{-1} in G, C and GC and at 2338 cm^{-1} in dG_{10}, dC_{10} and dG_{10}/dC_{10} disappears. New amine product bands appear in the area between 3000 cm^{-1} and 3500 cm^{-1} (spectra not shown here). The ketenimine band at 2170 cm^{-1} in dC_{10} and dG_{10}/dC_{10} disappears as well. B: Reaction of isocyanate photo-products with water vapour. The isocyanate band at 2338 cm^{-1} in T, AT, dT_{10} and dA_{10}/dT_{10} and the ketenimine band at 2170 cm^{-1} in T and dT_{10} disappear. New amine product bands appear in the area between 3000 cm^{-1} and 3500 cm^{-1} for dT_{10} (spectra not shown here).

Table S1: Vibrational assignment of IR bands in the G film (calculations are scaled with 0.957)

spectral position		vibrational assignment
experiment / cm^{-1}	calculation / cm^{-1}	
3492	3545	free N-H stretch of H-bonded NH_2 group
3478	3528	NH_2 stretch, free
3440	3428	N(1)-H stretch, free
3304	3366	N-H stretch of H-bonded NH_2
3133	3097	N(1)-H stretch – H-bonded and C(8)-H stretch
2953	2962	C-H stretch, sugar – protection groups
2928	2914	C-H stretch, sugar – protection groups
2899	2891	C-H stretch, sugar
2857	2836	C-H stretch, sugar
1693	1693	C=O stretch, H-bonded
1628	1598	N-H bending of free NH_2
1595	1568	N(1)-H, NH_2 bending – H-bonded
1534	1517	C(4)=N(3) stretch
1472	1458	C-N stretch, ring
1253	1244	C-H bending, sugar- protection groups

Table S2: Vibrational assignment of IR bands in the C film (calculation are scaled with 0.957)

spectral position		vibrational assignment
experiment / cm^{-1}	calculation / cm^{-1}	
3491	3521	N-H stretch – free of H-bonded NH_2
3127	3090	N-H stretch – H-bonded NH_2
2954	2966	C-H stretch; sugar – protection groups
2929	2922	C-H stretch; sugar – protection groups
2889	2891	C-H stretch, sugar
2858	2836	C-H stretch, sugar
1663	1663	C=O stretch
1630	1629	N-H_2 bending ; C=C stretch, ring
1575	1593	N-H_2 bending ; C=C stretch, ring
1487	1486	C-C stretch, ring
1473	1465	C-N stretch, ring
1362	1349	skeleton vibration
1254	1245	C-H bending, sugar- protection groups

Table S3: Vibrational assignment of IR bands in the T film (calculation are scaled with 0.957)

spectral position		vibrational assignment
experiment / cm^{-1}	calculation / cm^{-1}	
3403	3435	N(3)-H stretch
3053	3070	C(6)-H stretch
2829	2877	C-H stretch, sugar
1694	1685	C(2)=O stretch
1665	1672	C(4)=O stretch, N(3)-H bending
1476	1405	C(1')-H bending
1277	1237	C-H bending
1096	1076	skeleton vibration
1054	1048	C-O sugar

Table S4: Vibrational assignment of IR bands in the A film (calculation are scaled with 0.993)

spectral position		vibrational assignment
experiment / cm^{-1}	calculation / cm^{-1}	
3333	3331	C(2') O-H stretch
2924	2989	C-H stretch, sugar
1646	1646	NH_2 bending
1602	1607	NH_2 bending
1577	1595	C-N ring, NH_2 bending
1507	1520	C(8)-H bending, C-N ring
1478	1494	C(2)-H bending
1421	1379	skeleton vibration
1372	1355	skeleton vibration
1333	1321	C(1')-H, C(4')-H bending
1299	1270	skeleton vibration
1262	1242	C(5‘)-O bending, C-H bending sugar
1247	1216	C-H bending
1207	1185	skeleton vibration
1173	1130	skeleton vibration
1121	1078	C-C ring sugar
1086	1046	C(5‘)-O stretch
1054	1022	skeleton vibration
1014	955	skeleton vibration

Quantum Yields

The total quantum yield of photo-reaction Φ_{tot} is defined as the number of reacted molecules $N_{reac.Ed.}$ divided by the number of absorbed photons N_{abs}.

$$\Phi_{\mathrm{tot}} = \frac{N_{reac.Ed.}}{N_{abs}} = \frac{\frac{\Delta A}{A} \cdot N_{illum.}}{E_{abs} \cdot Z \cdot \frac{\lambda}{h \cdot c}}$$

Here $N_{illum.}$ is the number of molecules in the illumination area, which can be calculated from the amount of substance on the whole film, the film thickness and the illumination area. λ is the irradiation wavelength (266 nm), c the light velocity and h the Planck constant. Z is the number of laser pulses and E_{abs} the energy absorbed by the sample per laser pulse, which is determined for each film separately. A is the absorbance of the film before illumination at a specific wavelength of an isolated educt marker band. The difference absorption ΔA is determined from the difference spectra. ΔA/A is the percentage of reacted educt molecules. The temporal evolution of the negative difference bands is fitted biexponentially. The first time constant τ_1 is assigned to photo-reaction, the second time constant τ_2 to photo-damage by thermal effects and laser desorption [44]. To correct the difference absorbance for the photo-damage, monoexponential curves with the time constant τ_1 and the corresponding amplitude A_1 from the biexponential fit are calculated. The difference absorption ΔA of these curves is used for the quantum yield calculation.

To obtain the isocyanate quantum yield $\Phi_{N=C=O}$, the absorption coefficient of the resulting product is needed. Therefore a calibration with 1,4-phenylenediisocyanate (PDICy) is used.

$$\frac{I_{calc.product}}{I_{calc.PDICy}} = \frac{\varepsilon_{product}}{\varepsilon_{PDICy}}$$

From the ratios of the calculated integrated absorption coefficients *I* of the possible isocyanate photo-products and of 1,4-phenylenediisocyanate (PDICy) and from the experimental extinction coefficients ε_{PDICy}, $\varepsilon_{product}$ can be calculated. The isocyanate quantum yield can then be determined as follows,

$$\Phi_{\mathrm{N=C=O}} = \frac{c_{N=C=O} \cdot V_{illum.} \cdot N_A}{E_{abs} \cdot Z \cdot \frac{\lambda}{h \cdot c}}$$

with $V_{illum.}$ as the volume of the film which is illuminated, N_A as Avogadro constant and $c_{C=N=O}$ as isocyanate concentration. The concentration can be calculated from the Lambert-Beer law, with the absorbance at 2277 cm^{-1} or 2338 cm^{-1}, respectively.

Furthermore the quantum yield for the imino-oxo tautomer $\Phi_{imino\text{-}oxo}$ is calculated. The extinction coefficient $\varepsilon_{imino\text{-}oxo}$ is determined from the ratios between the calculated intensities of the imino-oxo products, the isocyanate products and the isocyanate extinction coefficient.

$$\frac{I_{calc.\ imino-oxo}}{I_{N=C=O}} = \frac{\varepsilon_{calc.\ imino-oxo}}{\varepsilon_{N=C=O}}$$

$$\Phi_{\mathrm{imino-oxo}} = \frac{c_{imino-oxo} \cdot V_{illum.} \cdot N_A}{E_{abs} \cdot Z \cdot \frac{\lambda}{h \cdot c}}$$

The concentration $c_{imino\text{-}oxo}$ is determined from the Lambert-Beer law as described above by using the absorbance of the C=N stretch vibration around 1640 cm^{-1} in G.